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Jörg Bünemann

Group Theory in Physics

An Introduction with a Focus on Solid State Physics

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Jörg Bünemann

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An Introduction with a Focus on Solid State Physics

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Preface

I would like to share with the reader the unusual story behind this book's genesis. During my time as a diploma and doctoral student at TU Dortmund University, I first encountered group theoretical questions in solid-state physics. Among the books available to me at that time, I particularly admired the German version of Hans-Waldemar Streitwolf's 1965 book, which was later published in English as 'Group Theory in Solid-State Physics'. When I began lecturing on this topic, I found that my appreciation for Streitwolf's book had not diminished. It contained, for example, a beautiful proof of an essential theorem (Equation (5.10) in this book) which most other books on the subject did not prove at all.

In 2016, I found out by chance that Streitwolf, like me at that time, was living in Berlin in the best of health, despite his advanced age of 90. So I contacted him and we met for coffee in Berlin-Mitte. During our conversation, he shared with me how his book came about, in a way that would be impossible today. As was not uncommon in the GDR (the communist eastern part of Germany) during the 1960s, Streitwolf received a permanent position at a scientific academy after completing his Ph.D. When he asked his new supervisor what he should do first, the response was that he should write a book about group theory in solid-state physics. Streitwolf objected, saying he knew nothing about the subject. However, he was told by his supervisor to spend time on the subject and familiarize himself with it. Nowadays, it is unheard of that young postdocs write a textbook, particularly in a field that is completely new to them. Given the quality of Streitwolf's book, it raises some questions about the tradition that only people who have been working in their respective fields for decades usually write textbooks.

Initially, our plan was to publish an updated version of Streitwolf's book in English. Unfortunately, due to unresolved copyright issues around the English edition after 50 years, we were unable to proceed. Therefore, I decided to create a new book based on the lectures I have given on group theory at the Universities of Marburg, Cottbus, and Dortmund. Since this book draws heavily on Streitwolf's work, especially concerning the mathematics, I hope it will keep his legacy alive.

Primarily intended as a textbook for students new to the field, this book differs from most scholarly works on the subject. I recommend that readers start with Chaps. 1–8,

which are structured to build on each other. I have attempted to minimize the amount of mathematics used, including only what is absolutely necessary. In addition, I have moved the more mathematical concepts to where they are actually needed in the book, rather than overwhelming readers with too much mathematics at the beginning.

Since most proofs in group theory are relatively easy, I have included most of them in the book. I encourage readers to follow the proofs carefully, as this will help in their comprehension of the mathematical concepts and their applications in physics. I have also included exercises whose solutions can be found in Appendix B. It is highly recommended that readers engage in the exercises as this will be very helpful in understanding the rest of the book's content.

Despite every effort to avoid errors, given the length of this book it is probably inevitable that their number will not be zero. I document the errors that come to my attention on the following website:

https://cmt.physik.tu-dortmund.de/group-theory/.

Dortmund, Germany Jörg Bünemann

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Chapter 1
Introduction

1.1 A Brief Historical Overview

As we will discuss in the following Sect. 1.2, the fundamental relationship between physics and group theory is based on the fact that the set of symmetries of a physical system is, in the mathematical sense, a group.[1] The preoccupation with symmetries goes back to ancient times. Think, for example, of the 5 Platonic bodies (tetrahedron, cube, octahedron, dodecahedron, icosahedron), whose faces are made of identical regular polygons. We will discuss these bodies in Chap. 3, since their symmetries are determined by certain *point groups*. Point groups will turn out to be of great importance in solid-state physics.

Although, as we know today, group theory plays a major role in various mathematical disciplines such as number theory or geometry, the formal concept of a group emerged rather late at the beginning of the 19th century. Worth mentioning here in particular is Evariste Galois, who realized around 1831 that the solutions of algebraic equations are closely related to the so-called *permutation groups*. Since Galois died only shortly afterwards, at the age of just 20, his findings remained largely unknown for quite some time and were only taken up again in the second half of the 19th century by Camille Jordan. Between 1860 and 1880, Jordan developed the essential principles of permutation groups. From these works, but also through personal encounters, two other important protagonists were attracted by the field of group theory—the somewhat younger mathematicians Felix Klein and Sophus Lie. Klein published the so-called *Erlanger Programm*,[2] which consisted of clarifying and formalizing the fundamentals of geometry by focusing on the symmetries of geometric objects. This program had a great influence on the development of geometry. Lie is best known for his work in the area of Lie groups and Lie algebras. He developed the theory of continuous transformation groups (now known as Lie groups). These

[1] We define groups in Sect. 2.1.

[2] Translated: Erlangen program.

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groups do have important applications in various areas of mathematics and theoretical physics. In the further development of the group theory and its connection with other mathematical fields, various mathematicians were involved, for whose detailed appreciation this brief introductory section is not a suitable place.[3]

In classical physics, group theory enables the systematic derivation of conservation laws. Emmy Noether's famous theorem connects symmetries of physical systems with conserved quantities. For example, spatial translational symmetry leads to the conservation of momenta, as most readers probably have learned in their lecture on theoretical mechanics. Group theory also plays a role in classical electrodynamics, particularly in the formulation of Maxwell's equations. The invariance of these equations under Lorentz transformations described by the Poincar group is also of great importance in the theory of relativity.

Crystallography began in the 17th century with the first investigations of crystals by scientists such as Johannes Kepler. Later, early theories about the regular arrangement of particles in crystals were developed. The decisive breakthrough came in the late 19th century, when Wilhelm Conrad Röntgen discovered X-rays. These made it possible to introduce new methods for studying crystals. In 1912, Max von Laue showed that X-rays were diffracted by a crystal lattice. This led to the development of X-ray crystallography, which made it possible to determine the three-dimensional structure of crystals. Maurice L. Brillouin, a French physicist, contributed significantly to the application of group theory to crystallography in the 1920s. Brillouin recognized the importance of symmetries in crystals and used group theory to classify the different types of crystal symmetry operations. The German mathematician and crystallographer Friedrich H. Hermann developed a method for applying group theory to crystal structures in the 1920s. The so-called Hermann–Mauguin symbolism is still used today to describe the symmetry of crystals.

While group theory is primarily of mathematical and theoretical interest in classical physics, in quantum mechanics it also has considerable practical significance.[4] Of central importance here is the concept of the *representation* of a group (see Chap. 4). The beginnings of representation theory can be traced back to the end of the 19th century. The idea was first introduced by Ferdinand Frobenius and (independently) by William Burnside. Isaak Schur also contributed to the early work and played a crucial role in the further development of representation theory. He formulated, in particular, *Schur's lemma* (see Sect. 4.1.2), which is fundamental to the theory of *irreducible representations*.

The most important contributions to the introduction of group theory into quantum mechanics were probably made by Eugene Wigner and Hermanns Weyl. In particular Wigner will play a prominent role in this book. We introduce his projection operators in Sect. 6.2 and prove the famous Wigner–Eckart theorem in Chap. 10. In addition to solid-state physics, which we will primarily deal with in this book, group theory also

[3] Readers who are interested in more details, please refer to the following very comprehensive article: [1].

[4] At least in solid-state physics, the author has observed that experimental physicists are often more familiar with group theory than their theoretical counterparts.

plays an important role in elementary particle theory to this day. However, the groups relevant here are Lie groups, the study of which is a field in itself and is therefore not considered in this book.

1.2 Symmetries

In this Section, we delve into the mathematical concept of symmetries. We begin in Sect. 1.2.1 by discussing the symmetries of extended bodies, which are often helpful in visualization. Subsequently, in Sects. 1.2.2 and 1.2.3, we revisit the description of symmetries in classical physics and, more crucially, in quantum mechanics.

1.2.1 Symmetries of Bodies

It is often helpful to imagine symmetries using extended bodies. Mathematically, a body is a continuous set of spatial points, e.g. a ball, which consists of all points $\vec{r}$ with the property

$$|\vec{r}| \leq R \ .$$

A *symmetry transformation* is then a mapping of the point set into itself. As we will see in the following, only linear symmetry transformations are relevant for the physics which we consider in this book, i.e. transformations of the form

$$\vec{r} \to \vec{r}' = \tilde{D} \cdot \vec{r} + \vec{a} \tag{1.1}$$

with an orthogonal matrix $\tilde{D}$,

$$\tilde{D} \cdot \tilde{D}^T = \tilde{D}^T \cdot \tilde{D} = \tilde{1} \quad (\Rightarrow \tilde{D}^T = \tilde{D}^{-1})$$

and a constant vector $\vec{a}$. In infinitely extended crystals we must indeed consider symmetry transformations with non-vanishing vectors $\vec{a}$ (see Chap. 12 on space groups). In contrast, in finite bodies (corresponding to atoms or molecules in chemistry or physics) only the orthogonal transformations are relevant, since every symmetry transformation with $\vec{a} \neq \vec{0}$ is identical to an orthogonal transformation. In the case of a rectangle, for example, there is the orthogonal symmetry transformation of a π rotation around the red axis shown in Fig. 1.1. Equivalent to this, however, is the transformation shown in Fig. 1.2 where a π rotation and a translation are combined.

Example As an example of a three dimensional body, we consider the symmetries of a tetrahedron, shown in Fig. 1.3. There are three obvious types of symmetry transformations:

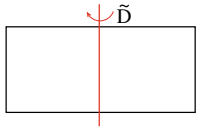

Fig. 1.1 Orthogonal symmetry transformation of a rectangle

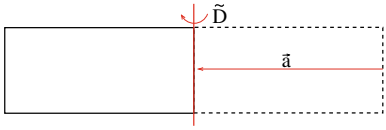

Fig. 1.2 Affine symmetry transformation of a rectangle

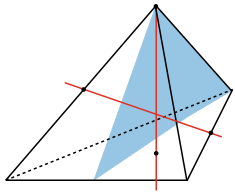

Fig. 1.3 Symmetry transformations of a tetrahedron

(i) $2\pi/3$ and $4\pi/3$ rotations around each axis through a corner and the opposite side's center.
(ii) π rotations around the centers of opposite edges.
(iii) Reflections on any plane that contains two vertices and the midpoints of opposite edges. Less obvious but also an orthogonal symmetry transformation are
(iv) $\pi/2$ and $3\pi/2$ rotations around the same axes as in (ii) multiplied with an inversion

$$\tilde{I} = -\tilde{1}$$

at the origin (*rotary inversion axes*).

It is now important that the successive execution $S_1 \circ S_2$ of two symmetry transformations S_1 and S_2 is also a symmetry transformation. This is the most important property of symmetries which will connect them with the group theory in the next chapters. As we will see, the operation $\circ$ also satisfies all other axioms of a group.

1.2.2 Symmetries in Classical Physics

A classical N-particle system is described by a Lagrangian

$$L(\{\vec{r}_l\}, \{\dot{\vec{r}}_l\}) = \sum_i^N \frac{1}{2} m_i \dot{\vec{r}}_i^{\,2} - V(\vec{r}_1, \ldots, \vec{r}_N) \ ,$$

where, e.g. $\{\vec{r}_l\}$ is an abbreviation for the set $\{\vec{r}_1, \ldots, \vec{r}_N\}$. A spatial symmetry transformation is then a transformation $\{\vec{r}_l\} \to \{\vec{r}_l{}'\}$ that leaves the form of L invariant, i.e.

$$L(\{\vec{r}_l(\{\vec{r}_l{}')\}\}, \{\dot{\vec{r}}_l(\{\vec{r}_l{}'\}, \{\dot{\vec{r}}_l{}'\})\}) \stackrel{!}{=} L(\{\vec{r}_l{}'\}, \{\dot{\vec{r}}_l{}'\}) \ .$$

Because of the terms $\sim \dot{\vec{r}}_i^{\,2}$, no non-linear transformations are conceivable here, but only the transformations introduced in (1.1). Time-dependent symmetry transformations, e.g. the time-dependent Galilei transformations, are not relevant in solid-state physics and will not be considered in this book. The symmetry of a body K can easily be generated in a physical system, for example by introducing a single-particle potential of the form

$$V(\vec{r}) = \begin{cases} V_0 \neq 0 \text{ if } \vec{r} \in K \\ 0 \quad \text{if } \vec{r} \notin K \end{cases} \ .$$

This will also be possible in quantum mechanics.

There are fields in classical physics in which symmetries (and thus group theory) play a role (e.g. in the elasticity theory). In this book, however, we will mainly deal with quantum mechanical systems.

1.2.3 Symmetries in Quantum Mechanics

In all applications, we only consider systems of a single-particle in an external potential throughout this book.[5] However, all essential statements on the relationship between group theory and symmetries in quantum mechanical systems are more generally valid. Single-particle systems are described by (normalized) wave functions

$$\Psi(\vec{r}) = \langle \vec{r} | \psi \rangle \ ,$$

with the spatial basis $|\vec{r}\rangle$ and a Hamiltonian

$$\hat{H} = \frac{\hat{\vec{p}}^{\,2}}{2m} + V(\hat{\vec{r}}) \ . \tag{1.2}$$

A spatial transformation of the form (1.1) corresponds to a transformation in the Hilbert space (of the square-integrable functions) $|\psi_1\rangle \to |\psi_2\rangle$, defined by

$$\Psi_1(\vec{r}\,') = \Psi_1(\tilde{D} \cdot \vec{r} + \vec{a}) \equiv \Psi_2(\vec{r}) \ .$$

[5] As most readers should be aware, a system of non-interacting electrons is described by Slater determinants arising from the corresponding single-particle problem. Therefore, the restriction to single-particle systems is not particularly restrictive in solid-state physics.

The corresponding operator $\hat{T}_{\tilde{D}}$ (for the sake of simplicity, we set $\vec{a} = \vec{0}$ in the following considerations) is then defined by the condition

$$\langle \vec{r}|\hat{T}_{\tilde{D}}|\psi\rangle \stackrel{!}{=} \langle \tilde{D}\cdot\vec{r}|\psi\rangle = \psi(\tilde{D}\cdot\vec{r}) \quad \forall|\psi\rangle \ . \tag{1.3}$$

The operator $\hat{T}_{\tilde{D}}$ is unitary because

$$\begin{aligned}\langle\psi|\hat{T}^{\dagger}_{\tilde{D}}\cdot\hat{T}_{\tilde{D}}|\psi\rangle &= \int \mathrm{d}^3r\langle\psi|\hat{T}^{\dagger}_{\tilde{D}}|\vec{r}\rangle\langle\vec{r}|\hat{T}_{\tilde{D}}|\psi\rangle \\ &= \int \mathrm{d}^3r|\psi(\tilde{D}\cdot\vec{r})|^2 = 1 \ .\end{aligned}$$

Since this equation is valid for all $|\psi\rangle$, it follows that

$$\hat{T}^{\dagger}_{\tilde{D}}\cdot\hat{T}_{\tilde{D}} = 1 \ ,$$

where (see Exercise 1)

$$\hat{T}^{\dagger}_{\tilde{D}} = \hat{T}^{-1}_{\tilde{D}} = \hat{T}_{\tilde{D}^{-1}} \ .$$

Before we come to the central theorem of this section, let us consider how the operators $\hat{T}_{\tilde{D}}$ act on the momentum space basis $|\vec{p}\rangle$:

$$\begin{aligned}\langle\vec{p}|\hat{T}_{\tilde{D}}|\psi\rangle &= \int \mathrm{d}^3r \ \underbrace{\langle\vec{p}|\vec{r}\rangle}_{=\frac{1}{\sqrt{V}}e^{-\mathrm{i}\vec{p}\cdot\vec{r}}} \ \underbrace{\langle\vec{r}|\hat{T}_{\tilde{D}}|\psi\rangle}_{=\langle\tilde{D}\cdot\vec{r}|\psi\rangle} \\ &\stackrel{(\vec{r}'\equiv\tilde{D}\vec{r})}{=} \int \mathrm{d}^3r'\frac{1}{\sqrt{V}}e^{-\mathrm{i}\vec{p}\cdot(\tilde{D}^{-1}\cdot\vec{r}')}\langle\vec{r}'|\psi\rangle \ .\end{aligned}$$

Since $\vec{p}\cdot(\tilde{D}^{-1}\cdot\vec{r}') = (\tilde{D}\cdot\vec{p})\cdot\vec{r}'$ we obtain the expected result

$$\langle\vec{p}|\hat{T}_{\tilde{D}}|\psi\rangle = \int \mathrm{d}^3r'\langle\tilde{D}\cdot\vec{p}|\vec{r}'\rangle\langle\vec{r}'|\psi\rangle = \langle\tilde{D}\cdot\vec{p}|\psi\rangle \ .$$

The essential connection to group theory is now provided by the following theorem: If $V(\vec{r})$ is invariant under the transformation $\tilde{D}$, i.e. $\tilde{D}$ is a symmetry of the system, then

$$[\hat{H}, \hat{T}_{\tilde{D}}] = 0 \ .$$

Proof We consider the two parts in the Hamiltonian (1.2) separately, first the kinetic energy,

$$\begin{aligned}\left[\frac{\hat{\vec{p}}^{\,2}}{2m}, \hat{T}_{\tilde{D}}\right] = 0 \quad &\Leftrightarrow \left\langle \vec{p}_1 \left| \frac{\hat{\vec{p}}^{\,2}}{2m}\hat{T}_{\tilde{D}} - \hat{T}_{\tilde{D}}\frac{\hat{\vec{p}}^{\,2}}{2m} \right| \vec{p}_2 \right\rangle = 0 \quad \forall \vec{p}_1, \vec{p}_2 \\ &= \left(\frac{\vec{p}_1^{\,2}}{2m} - \frac{\vec{p}_2^{\,2}}{2m}\right) \underbrace{\langle \vec{p}_1 | \hat{T}_{\tilde{D}} | \vec{p}_2 \rangle}_{= \langle \tilde{D}\cdot\vec{p}_1 | \vec{p}_2 \rangle = \delta(\tilde{D}\cdot\vec{p}_1 - \vec{p}_2)} \\ &= \left(\frac{\vec{p}_1^{\,2}}{2m} - \frac{(\tilde{D}\cdot\vec{p}_1)^2}{2m}\right) = 0 \,,\end{aligned}$$

where in the last step we have used that $(\tilde{D}\cdot\vec{p}_1)^2 = \vec{p}_1^{\,2}$ for an orthogonal matrix. The proof for the potential energy follows completely analogously with the only difference that one multiplies the commutator from left and right with spatial eigenstates $|\vec{r}_1\rangle$ and $|\vec{r}_2\rangle$.

We can now formulate more generally and beyond the one-particle Hamiltonian (1.2): In quantum mechanics, every unitary operator which commutes with $\hat{H}$ describes a symmetry transformation of the system. As in classical mechanics, the following also applies here: If $\hat{T}_1$, $\hat{T}_2$ are symmetry transformations, so is $\hat{T}_1 \cdot \hat{T}_2$, because $\hat{T}_1 \cdot \hat{T}_2$ is obviously also unitary and it is

$$[\hat{H}, \hat{T}_1 \cdot \hat{T}_2] = 0 \,.$$

This will lead to the connection with the group theory in the following chapters.

Example As an example, we consider the Hamiltonian (1.2) with a potential

$$V_1(\vec{r}) = \alpha_1 \cdot x + \alpha_2 \cdot y + \alpha_3 \cdot z \quad (\alpha_i \neq \alpha_j) \,.$$

The invariance under a rotational matrix $\tilde{D}$ then leads to

$$V_1(\vec{r}) \stackrel{!}{=} V_1(\tilde{D}\cdot\vec{r}) \;\Rightarrow\; \vec{\alpha}\cdot\vec{r} = \vec{\alpha}\cdot(\tilde{D}\cdot\vec{r}) = (\tilde{D}^{-1}\cdot\vec{\alpha})\cdot\vec{r} \tag{1.4}$$

where we have introduced the vector $\vec{\alpha}^T = (\alpha_1, \alpha_2, \alpha_3)$. The last equation in (1.4) means that $\tilde{D}$, $\tilde{D}^{-1}$ must be a rotation around the vector $\vec{\alpha}$. Examples of potentials that are more relevant in solid-state physics are discussed in Exercise 4.

Exercises

1. Prove that
$$\hat{T}_{\tilde{D}}^{-1} = \hat{T}_{\tilde{D}^{-1}} ,$$
for the operators defined in (1.3).
2. In this chapter it is shown that every linear transformation in position space corresponds to a unitary operator $\hat{T}$ in the Hilbert space (of the square-integrable functions). Show that the operator $\hat{T}$
   (a) for a pure translation $\vec{a}$ is given by
$$\hat{T}_{\vec{a}} = \exp\left(\frac{\mathrm{i}}{\hbar}\vec{a}\cdot\hat{\vec{p}}\right) ,$$
   and,
   (b) for a rotation around the z-axis with the angle α by
$$\hat{T}_{\alpha} = \exp\left(\frac{\mathrm{i}}{\hbar}\alpha\hat{L}_z\right) .$$
   Here $\hat{\vec{p}}$ is the momentum vector-operator and $\hat{L}_z$ the z component of the orbital angular momentum operator. What is the form of the unitary operator for a general rotation around a vector $\vec{\alpha}$ with the angle $\alpha = |\vec{\alpha}|$?
3. Show that each proper orthogonal matrix $\tilde{D}$ (proper meaning that the determinant is $|\tilde{D}| = 1$, see Chap. 3) actually causes a rotation about a certain rotation axis. In other words, show that there is an orthonormal basis $\vec{v}_i$ such that
$$D'_{i,j} \equiv \vec{v}_i^{\,T}\cdot\tilde{D}\cdot\vec{v}_j$$
has the form
$$\tilde{D}' = \begin{pmatrix} \cos(\varphi) & \sin(\varphi) & 0 \\ -\sin(\varphi) & \cos(\varphi) & 0 \\ 0 & 0 & 1 \end{pmatrix} .$$
   Here is a conceivable idea for this proof:
   (i) Show that $\tilde{D}$ has an eigenvector with eigenvalue 1, e.g. by proving that
$$|\tilde{1} - \tilde{D}| = 0 .$$
   (ii) Show that the two other (complex) eigenvalues have the form $e^{\mathrm{i}\varphi_i}$.
   (iii) Use the real and imaginary parts of the eigenvectors to find the vectors $\vec{v}_i$.

4. Consider the following potentials $V(\vec{r}) = V(x, y, z)$ in the Hamiltonian (1.2),

   (a)
   $$V_1(\vec{r}) = \alpha_1 \cdot x^2 + \alpha_2 \cdot y^2 + \alpha_3 \cdot z^2 \quad (\alpha_i \neq \alpha_j) \ ,$$

   (b)
   $$V_2(\vec{r}) = x \cdot y \cdot z^2 \ .$$

   Name the symmetries the Hamiltonian $\hat{H}$ has in both cases.

Reference

1. L. Bonolis, *From the Rise of the Group Concept to the Stormy Onset of Group Theory in the New Quantum Mechanics. A saga of the invariant characterization of physical objects, events and theories*, La Rivista del Nuovo Cimento **27**, 1, 2004.

Chapter 2
Groups: Definitions and Properties

In this chapter, we explore the fundamental properties of groups. We begin by defining groups in Sect. 2.1 and exploring some of their simple properties. In Sect. 2.2, we examine three finite groups, each represented by the symmetries of a geometric body. Finally, in Sect. 2.3, we introduce and discuss important concepts such as classes, (normal) sub-groups, and cosets.

2.1 Definition of Groups and Simple Properties

We start by defining groups. A *group* G is a set of elements, $a, b, c, \ldots$ (in the following sometimes also denoted as $a_1, a_2, \ldots$), having the following properties:

(1) A relationship called *group multiplication* is defined between the elements of the group, which assigns to every ordered pair of elements a, b an element $c = a \cdot b$ of the group. The element c is then denoted as the *product* of a and b.
(2) The multiplication satisfies the *associative law*

$$(a \cdot b) \cdot c = a \cdot (b \cdot c) \ .$$

(3) The group contains an *identity element*; that is, an element E such that

$$a \cdot E = E \cdot a = a \ ,$$

for every element a of the group.
(4) The group contains, for every element a, the corresponding *inverse element* a^{-1} with the defining property

$$a \cdot a^{-1} = a^{-1} \cdot a = E \ .$$

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Table 2.1 Left: multiplication table of the only group C_2 of order $g = 2$; Right: A $g = 2$ multiplication table which violates the group axioms.

	E	a
E	E	a
a	a	E

	E	a
E	E	a
a	E	a

In Exercise 1, the reader may show that both the identity element and the inverse element of an element are unique. Another task in that exercise is to show that axiom (4) can be formulated more weakly.

In our group definition, we have already assumed that the group elements can be counted, since we will only deal with such groups in this book. Of course, there also exist groups that are uncountable, such as the group $O(3)$ which consists of all orthogonal matrices. A group G is denoted as *finite* if it contains a finite number of elements, and the number g of elements in a group is referred to as the *order* of G. In solid-state physics, all relevant groups are finite, or can be made finite by introducing periodic boundary conditions.

A finite group is described by its *multiplication table* or *group table*, which enumerates the product of every pair of elements in the group. For instance, the only group of order $g = 2$ (referred to as C_2) has a multiplication table displayed in Table 2.1 (left). In the group table, the first column (line) exhibits the first (second) factor a (b), and the corresponding product $c = a \cdot b$ is shown in the table.

The statement that there exists only one group for $g = 2$ actually requires an additional definition: Two groups G and G' are considered as identical if they are *isomorphic* ($G \widehat{=} G'$); i.e. if there is a bijective mapping

$$f : G \leftrightarrow G' \ ,$$

such that

$$f(a \cdot b) = f(a) \cdot f(b) \ , \tag{2.1}$$

for all $a, b \in G$. If another group of order $g = 2$ existed, it would have a different multiplication table, e.g. the one in Table 2.1 (right). This table, however, is not consistent with the assumed order of the group, since, if we multiply $a \cdot a = a$ with a^{-1} it follows $a = E$. This means that the set would have only one and not two elements ($g = 1$).

A group G is said to be *Abelian* if the multiplication satisfies the commutative law

$$a \cdot b = b \cdot a \qquad \forall a, b \in G \ .$$

Obviously, an Abelian group (and only an Abelian group) has a symmetric multiplication table with respect to a reflection on the diagonal.

Table 2.2 Number of groups $N(g)$ and Abelian groups $N_a(g)$ for various values of the group order g

g	1	2	3	4	5	6	7	8	10	12	24	48
$N(g)$	1	1	1	2	1	2	1	5	2	5	15	32
$N_a(g)$	1	1	1	2	1	1	1	3	1	2	3	5

The smallest integer number n with

$$a^n \equiv \underbrace{a \cdot a \cdot \ldots a}_{\text{n elements}} = E \ ,$$

is called the *order of the element*. In finite groups, an order can be assigned to every element.

Proof We define the series of group elements

$$b_1, b_2, \ldots, b_i \ldots \equiv a, a^2, \ldots, a^i \ldots \ .$$

In a finite group, it must be $b_i = b_j$ for some $j > i$. Then we can conclude[1]

$$a^i = a^j|_{\cdot (a^{-1})^i} \Rightarrow \ a^i \cdot (a^{-1})^i = a^j \cdot (a^{-1})^i \Rightarrow E = a^{j-i} \ . \ \surd \qquad (2.2)$$

A group G is denoted as *cyclic* if there is an element $a \in G$ that generates all other elements a_i in the group when raised to integer powers, $a_i = a^i$. The order of the generating element of a cyclic group is equal to the order of the group. Obviously, there exists exactly one cyclic group for every order g, and cyclic groups are always Abelian.

For a given order g, there is a finite number of groups $N(g)$ and a finite number of Abelian groups $N_a(g)$. The numbers of groups and Abelian groups for some orders g are shown in Table 2.2. There is at least one Abelian group for every order, which is the cyclic group of that order. The smallest order with more than one group is $g = 4$, and the smallest non-Abelian group has the order $g = 6$. We will discuss these three groups in the following section.

2.2 Examples

As examples, we consider the groups D_2, C_4 (both $g = 4$) and D_3 ($g = 6$).[2]

[1] The bar in (2.2) means that both sides of the equation are multiplied with $(a^{-1})^i$ from the right.

[2] The notations for point groups, such as D_2, are introduced systematically in Chap. 3.

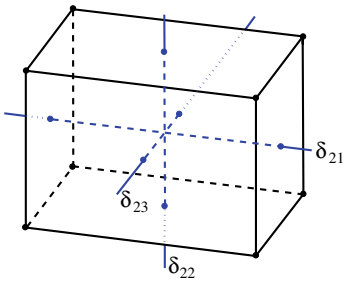

Fig. 2.1 Symmetry group D_2: Cuboid with edges of unequal length

2.2.1 The Group D_2

The dihedral group, denoted as D_2, is a group of order $g = 4$.[3] We imagine groups to take the form of certain spatial transformations (for example, rotations and reflections). Specifically, it can be seen as the set of rotations in space that map a cuboid with unequal edge lengths onto itself (see Fig. 2.1). Here we deliberately ignore the other symmetries that also exist in this body, such as the mirror planes. Excluding the identity transformation, there are three rotations through π about the axes δ_{2i} where $i = 1, 2, 3$. These axes are called *twofold rotational axes* or *twofold axes of symmetry* because repeating a rotation through π about a coordinate axis results in the identity transformation. We will use δ to denote elements corresponding to rotations throughout this manuscript (e.g. δ_{21}), where the first subscript represents the order of the element and the second one counts the axis of rotation if there is more than one. The orientation of a rotation axis can be arbitrarily chosen, which may result in a different multiplication table arrangement. However, two groups defined with different orientations are isomorphic, meaning that they are identical according to our definition of identical groups.

We can now readily set up the multiplication table for D_2,[4] see Table 2.3. The group D_2 is obviously Abelian because the multiplication table is symmetric. Every element is its own inverse. Hence, the main diagonal contains only the identity element. The group is not cyclical because no element δ_{2i} is the square of another one.

2.2.2 The Cyclic Group C_4

The second group of order 4 is the cyclic group C_4. Its elements can be regarded as corresponding to all the rotations which leave unchanged a right square pyramid

[3] Historically, this group, introduced by Felix Klein in 1884 for the first time, was also called *Vierergruppe*.

[4] In the next section, we describe how to practically set up a multiplication table using the more complicated group D_3 as an example.

Table 2.3 Multiplication table of the dihedral group D_2

	E	δ_{21}	δ_{22}	δ_{23}
E	E	δ_{21}	δ_{22}	δ_{23}
δ_{21}	δ_{21}	E	δ_{23}	δ_{22}
δ_{22}	δ_{22}	δ_{23}	E	δ_{21}
δ_{23}	δ_{23}	δ_{22}	δ_{21}	E

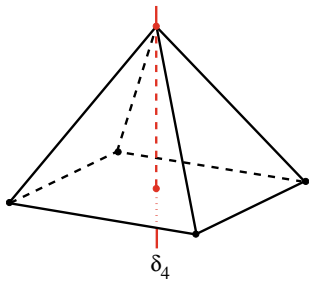

Fig. 2.2 Symmetry group C_4: right square pyramid

Table 2.4 Multiplication table of the cyclic group C_4

	E	δ_4	δ_4^2	δ_4^3
E	E	δ_4	δ_4^2	δ_4^3
δ_4	δ_4	δ_4^2	δ_4^3	E
δ_4^2	δ_4^2	δ_4^3	E	δ_4
δ_4^3	δ_4^3	E	δ_4	δ_4^2

(see Fig. 2.2). These are the powers ($\delta_4^2, \delta_4^3, \delta_4^4 = E$) of the rotation δ_4 about the fourfold axis of the pyramid. The multiplication table of C_4 is as shown in Table 2.4. The group C_4, being cyclic, is necessarily Abelian. Note that

$$\delta_4^{-1} = \delta_4^3 \quad , \quad \left(\delta_4^3\right)^{-1} = \delta_4 \ .$$

2.2.3 *The Group D_3*

The group D_3 is the simplest non-Abelian group and has the order $g = 6$. It can be visualized by the set of all rotations that preserve a prism with the base of an equilateral triangle (again excluding reflection symmetries and the inversion).[5] These

[5] For the sake of completeness it should be mentioned that D_3 is isomorphic to the group S_3 of permutations of a set with three-elements (see Exercise 11). In mathematics books, the permutation groups are usually dealt with extensively. For our applications in this book, however, they are irrelevant.

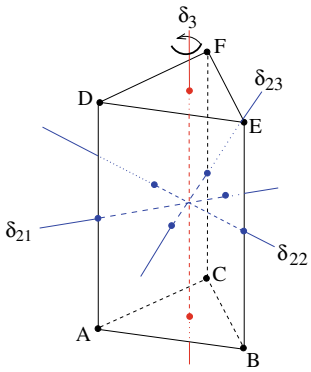

Fig. 2.3 Symmetry group D_3: leaves a prism with the base of an equilateral triangle invariant

rotations include those about a threefold axis perpendicular to the triangles, and those about three twofold axes passing through the centers of opposing edges and sides. The group D_3 is composed of six elements, namely E, δ_3, δ_3^2, δ_{21}, δ_{22}, and δ_{23}, as shown in Fig. 2.3. Setting up the multiplication table is not as straightforward as in the previous examples. We consider the rotation axes as fixed in space and need to find out at which position the three corners $A, \ldots, F$ are positioned after two rotations have been carried out. As an example, we want to show that $\delta_{21} \cdot \delta_3 = \delta_{22}$. To this end, we consider the two successive transformations

$$\begin{pmatrix} A \\ B \\ C \\ D \\ E \\ F \end{pmatrix} \xrightarrow{\delta_3} \begin{pmatrix} C \\ A \\ B \\ F \\ D \\ E \end{pmatrix} \xrightarrow{\delta_{21}} \begin{pmatrix} F \\ E \\ D \\ C \\ B \\ A \end{pmatrix} . \tag{2.3}$$

Here the 6 positions in the vectors correspond to the 6 spatially fixed positions of the vertices of the prism. The same rotation as in (2.3) is given by δ_{22} , i.e.

$$\begin{pmatrix} A \\ B \\ C \\ D \\ E \\ F \end{pmatrix} \xrightarrow{\delta_{22}} \begin{pmatrix} F \\ E \\ D \\ C \\ B \\ A \end{pmatrix} .$$

As mentioned before the direction of the rotations can be chosen arbitrarily. Our choice leads to a multiplication table that is shown in Table 2.5. The six elements have the following orders

Table 2.5 Multiplication table of the group D_3

	E	δ_3	δ_3^2	δ_{21}	δ_{22}	δ_{23}
E	E	δ_3	δ_3^2	δ_{21}	δ_{22}	δ_{23}
δ_3	δ_3	δ_3^2	E	δ_{23}	δ_{21}	δ_{22}
δ_3^2	δ_3^2	E	δ_3	δ_{22}	δ_{23}	δ_{21}
δ_{21}	δ_{21}	δ_{22}	δ_{23}	E	δ_3	δ_3^2
δ_{22}	δ_{22}	δ_{23}	δ_{21}	δ_3^2	E	δ_3
δ_{23}	δ_{23}	δ_{21}	δ_{22}	δ_3	δ_3^2	E

$$\begin{aligned}&\text{order } n = 1 : E \ ,\\ &\text{order } n = 2 : \delta_{21} \ , \ \delta_{22} \ , \ \delta_{23} \ ,\\ &\text{order } n = 3 : \delta_3 \ , \ \delta_3^2 \ .\end{aligned}$$

As the simplest non-Abelian group, we will encounter the group D_3 and its multiplication table in a number of sections in this book.

2.3 Classes of Conjugate Elements, Subsets, and Cosets

2.3.1 The Rearrangement Theorem

A simple, but very useful statement is the *rearrangement theorem*. It states that, for all finite groups $G = \{a_1, \ldots, a_g\}$ and any element $a \in G$, we have

$$G' \equiv a \cdot G \equiv \{a \cdot a_1, \ldots, a \cdot a_g\} = G \ . \tag{2.4}$$

Here, the last equation indicates that both sides of the equation refer to the same set of elements, disregarding their order. In other words, multiplying all elements of a group with one of its elements only rearranges the group. Consequently, in every row and column of a multiplication table, all the elements of the group are present, as already demonstrated in our three examples in Sect. 2.2.

Proof Let us assume that not all of the elements of G were contained in G'. In that case, at least two of the elements of G' (e.g. the elements $a \cdot a_i$ and $a \cdot a_j$ with $i \neq j$) had to be the same. Then, however, we find

$$a \cdot a_i = a \cdot a_j \Rightarrow \underbrace{a^{-1} \cdot a}_{=E} \cdot a_i = \underbrace{a^{-1} \cdot a}_{=E} \cdot a_j \Rightarrow a_i = a_j \ ,$$

which contradicts the assumption that $i \neq j$ $\quad \surd$

2.3.2 Definition and Properties of Classes

Two elements $a, b \in G$ are said to be *conjugate* ($a \sim b$) if and only if there exists an element $c \in G$ such that $a = c^{-1} \cdot b \cdot c$. This defines what mathematicians call an *equivalence relationship* because it is reflexive

$$a \sim a \ ,$$

symmetric

$$a \sim b \Leftrightarrow b \sim a \ ,$$

and transitive

$$a \sim b \ \text{ and } \ a \sim c \ \Rightarrow \ b \sim c \ . \tag{2.5}$$

Proof The symmetry is obvious. That $a \sim a$ follows with $c = E$. If $a \sim b$ and $a \sim c$ there are group elements x, y such that

$$a = x^{-1} \cdot b \cdot x = y^{-1} \cdot c \cdot y \ .$$

Multiplying the right equation from left(right) with $x(x^{-1})$ yields

$$b = \underbrace{(x \cdot y^{-1})}_{=z^{-1} \in G} \cdot c \cdot \underbrace{(y \cdot x^{-1})}_{\equiv z \in G} \ ,$$

which means that $b \sim c$. Here we have used that

$$(a \cdot b)^{-1} = b^{-1} \cdot a^{-1} \ . \ \surd$$

Due to (2.5) the conjugacy relationship defines a division of G into *classes of conjugate elements* (or simply *classes*); the number r of classes in G is called the *class number*. A consequence of this is that a and $c^{-1} \cdot a \cdot c$ are in the same class for all $c \in G$, with the special case $a = c^{-1} \cdot a \cdot c$.

For example, as one can show with the multiplication Table 2.5, the group D_3 contains $r = 3$ classes $\mathcal{C}_i$, $i = 1, \ldots, r$.[6]

$$D_3 = \sum_{i=1}^{3} \mathcal{C}_i = \mathcal{C}_1 \cup \mathcal{C}_2 \cup \mathcal{C}_3 \ ,$$

[6] Here, and throughout this work, sums are often taken in the sense of set unification, i.e. it is

$$\sum_l \equiv \cup_l$$

.

with

$$\mathcal{C}_1 = \{E\} \ , \ \mathcal{C}_2 = \{\delta_3, \delta_3^2\} \ , \ \mathcal{C}_3 = \{\delta_{21}, \delta_{22}, \delta_{23}\} \ .$$

Let us now consider some further properties of classes of conjugate elements. In Abelian groups, every element is a class by itself because

$$b = c^{-1} \cdot a \cdot c \Rightarrow b = a \cdot c^{-1} \cdot c = a \ .$$

The number of classes is then equal to the order of the group, $r = g$. The identity element is always a class by itself because, if $E \sim a$, it follows

$$E = c^{-1} \cdot a \cdot c|_{c\cdot(\ldots)\cdot c^{-1}} \Rightarrow E = a \ ,$$

where we have multiplied the left equation from left/right with c/c^{-1}. Elements in the same class have the same order (as defined in Sect. 2.1). For, if a and

$$b = c^{-1} \cdot a \cdot c$$

are conjugate elements and if the order of a is n, then

$$E = a^n = (c^{-1} \cdot b \cdot c)^n = \underbrace{(c^{-1} \cdot b \cdot c)(c^{-1} \cdot b \cdot c) \ldots (c^{-1} \cdot b \cdot c)}_{\text{n elements}} = c^{-1} \cdot b^n \cdot c|_{c\cdot(\ldots)\cdot c^{-1}} \Rightarrow b^n = E \ .$$

Thus, a class includes only rotations about axes of the same order. The converse is not valid. Two elements having the same order may well belong to different classes. For example, the elements δ_{21} and δ_{22} of the group D_2 are both of order 2 but belong to different classes since they are elements of an Abelian group.

The inverse class $\mathcal{C}_{\tilde{i}}$ of $\mathcal{C}_i$ consists (by definition) of the inverse elements of $\mathcal{C}_i$. This is, in fact, a class, because if, with $a, b \in \mathcal{C}_i$ and $c \in G$,

$$a = c^{-1} \cdot b \cdot c \ ,$$

then it also holds

$$a^{-1} = \left(c^{-1} \cdot b \cdot c\right)^{-1} = c^{-1} \cdot b^{-1} \cdot c \cdot \ \surd$$

It can happen that $\mathcal{C}_{\tilde{j}} = \mathcal{C}_j$, as it is the case, for example, for all classes of the group D_3.

We can formulate another rearrangement theorem, this time for classes: Let $C = \{b_1, \ldots, b_m\}$ be a class in G and $a \in G$. Then it is

$$\{a^{-1} \cdot b_1 \cdot a, \ldots, a^{-1} \cdot b_m \cdot a\} = C \ . \tag{2.6}$$

Proof With $b_i \in \mathcal{C}$ it is also $d_i \equiv a^{-1} \cdot b_i \cdot a \sim b_i \in \mathcal{C}$. The rearrangement theorem, however, tells us that all elements on the left-hand side of (2.6) are different, which proves this equation. $\surd$

At this point, the division of a group into classes may appear as a relatively abstract matter for the reader. However, in later chapters it will turn out to be a central concept, as far as the relationship between group theory and physics is concerned.

2.3.3 Class Multiplication

If $\mathcal{C}_1, \ldots, \mathcal{C}_r$ are the classes of a group G with $r_1, \ldots, r_r$ elements, respectively,[7] then a product $\mathcal{C}_i \cdot \mathcal{C}_j$ of two classes $\mathcal{C}_i = \{a_1, \ldots, a_{r_i}\}$ and $\mathcal{C}_j = \{b_1, \ldots, b_{r_j}\}$ is defined as[8]

$$\begin{aligned} \mathcal{C}_i \cdot \mathcal{C}_j &= \sum_{\gamma,\beta} a_\gamma \cdot b_\beta \\ &= \{a_1 \cdot b_1, \ldots, a_1 \cdot b_{r_j}, a_2 \cdot b_1, \ldots, a_{r_i} \cdot b_{r_j}\} . \end{aligned}$$

The product is a set of $r_i \cdot r_j$ elements, which, in general, are not all distinct. Then, the following theorem holds: The set $\mathcal{C}_i \cdot \mathcal{C}_j$ consists of entire classes of G and we may write (see footnote 6)

$$\mathcal{C}_i \cdot \mathcal{C}_j = \sum_{k=1}^{r} f_{ijk} \mathcal{C}_k \, . \tag{2.7}$$

The *class multiplication coefficients* f_{ijk} are positive integers or zero. Here, as in many other places in this book, the sum in (2.7) is to be understood as a union of sets, where, for example, $2 \cdot \mathcal{C}_k$ means that the class $\mathcal{C}_k$ appears twice.

Proof We must show that, if a occurs n times in $\mathcal{C}_i \cdot \mathcal{C}_j$, then the entire class $\mathcal{C}_k$ containing a also occurs n times in $\mathcal{C}_i \cdot \mathcal{C}_j$. If a occurs n times in $\mathcal{C}_i \cdot \mathcal{C}_j$, there must be n different pairs $a_\lambda^{(i)} \in \mathcal{C}_i, a_\lambda^{(j)} \in \mathcal{C}_j$ with

$$a_\lambda^{(i)} \cdot a_\lambda^{(j)} = a \quad (\lambda = 1, \ldots, n).$$

Now, if $\mathcal{C}_k$ is generated from a by the elements b_l $(l = 1, \ldots, r_k)$ such that

$$\mathcal{C}_k = \sum_{l=1}^{r_k} b_l^{-1} \cdot a \cdot b_l \, ,$$

then the elements

[7] The reader should not be confused by the fact that we (following Streitwolf) use the letter r as the class number and at the same time denote r_i as the number of elements in the class $\mathcal{C}_i$.

[8] We introduce the class multiplication only because it will be needed in a central proof in Sect. 5.2.2. Apart from that, it is of no importance in this book and it is, therefore, also not discussed in most textbooks on group theory in physics. Readers who are less interested in mathematics may therefore skip this section.

$$b_l^{-1} \cdot a \cdot b_l = b_l^{-1} \cdot a_\lambda^{(i)} \cdot a_\lambda^{(j)} \cdot b_l = \underbrace{b_l^{-1} \cdot a_\lambda^{(i)} \cdot b_l}_{\in \mathcal{C}_i} \cdot \underbrace{b_l^{-1} \cdot a_\lambda^{(j)} \cdot b_l}_{\in \mathcal{C}_j} \quad (\lambda = 1, \ldots, n)$$

form the class $\mathcal{C}_k$ n times and are contained in $\mathcal{C}_i \cdot \mathcal{C}_j$. $\surd$

In Sect. 5.2.2 we will need an expression for f_{ij1} where $\mathcal{C}_1 \equiv \{E\}$. Obviously, it is $f_{ij1} \neq 0$ only if $j = \bar{i}$, i.e. if $\mathcal{C}_j$ is the inverse class of $\mathcal{C}_i$. The class $\mathcal{C}_1$ then appears in $\mathcal{C}_i \cdot \mathcal{C}_{\bar{i}}$ exactly r_i times, namely whenever an element from $\mathcal{C}_i$ is multiplied with its inverse in $\mathcal{C}_{\bar{i}}$. Mathematically this means[9]

$$f_{ij1} = r_i \cdot \delta_{i,\bar{j}} = r_{\bar{i}} \cdot \delta_{i,\bar{j}} \; . \tag{2.8}$$

Example As an example, we consider the group D_3. The multiplication of the class $\mathcal{C}_2 = \mathcal{C}_{\bar{2}}$ with itself yields

$$\begin{aligned} \mathcal{C}_2 \cdot \mathcal{C}_2 &= \{\delta_3 \cdot \delta_3, \delta_3 \cdot \delta_3^2, \delta_3^2 \cdot \delta_3, \delta_3^2 \cdot \delta_2^3\} \\ &= \{\delta_3^2, E, E, \delta_3\} = \mathcal{C}_2 + 2\mathcal{C}_1 \; . \end{aligned}$$

In the same way, one finds (see Exercise 2)

$$\mathcal{C}_1 \cdot \mathcal{C}_i = \mathcal{C}_i \; , \; \mathcal{C}_2 \cdot \mathcal{C}_3 = 2\mathcal{C}_3 \; , \; \mathcal{C}_3 \cdot \mathcal{C}_3 = 3\mathcal{C}_1 + 3\mathcal{C}_2 \; . \tag{2.9}$$

2.3.4 *Sub-groups and Cosets*

A subset G' of a group G is called a *sub-group of* G if its elements themselves satisfy the group axioms with the same multiplication rules as in G. This means in particular that $E \in G'$ and if $a, b \in G'$ then also $a \cdot b \in G'$. According to this definition, trivial sub-groups of G are always $\{E\}$ and G itself. In D_3,

$$\{E, \delta_3, \delta_3^2\} \quad \text{and} \quad \{E, \delta_{2i}\} \quad (i = 1, 2, 3) \; ,$$

are non-trivial sub-groups. On the other hand, however, the set $G' = \{E, \delta_{21}, \delta_{22}, \delta_{23}\}$ is not a sub-group since, for example, $\delta_{21} \cdot \delta_{22} = \delta_3 \notin G'$.

Let G' be a sub-group of G of order g' and $a \in G$. Then the set

$$L_a \equiv \{a \cdot a_1, \ldots a \cdot a_{g'}, \} = a \cdot G' \; ,$$

[9] Here we use the standard Kronecker symbol

$$\delta_{i,j} = \begin{cases} 1 \text{ if } i = j \\ 0 \text{ if } i \neq j \end{cases} \; .$$

with also g' elements is called a *left coset of* G'. The following holds: two left cosets L_a and L_b (with $a \neq b$) are either identical or have no common elements.

Proof Let L_a and L_b be given where $a \neq b$. Suppose, contrary to the assertion, that there are elements $c_1, c_2 \in G$, for which

$$c_1 \in L_a, L_b \ , \tag{2.10}$$
$$c_2 \in L_a \ \text{ and } \ c_2 \notin L_b \ , \tag{2.11}$$

where (2.11) implies that the sets L_a and L_a are not identical. Then, because of (2.10), elements $d_1, d_2 \in G'$ exist with

$$c_1 = a \cdot d_1 \ , \tag{2.12}$$
$$c_1 = b \cdot d_2 \ . \tag{2.13}$$

This results in

$$a = c_1 \cdot d_1^{-1} \overset{(2.13)}{=} b \cdot d_2 \cdot d_1^{-1} \ . \tag{2.14}$$

Analogously, because of (2.11), there is a group element $d_1' \in G'$ with

$$c_2 = a \cdot d_1' \overset{(2.14)}{=} b \cdot \underbrace{d_2 \cdot d_1^{-1} \cdot d_1'}_{\in G'} \ .$$

Thus $c_2 \in L_b$ in contradiction to the assumption in (2.11). $\surd$

We can summarize as follows: Each sub-group G' of G induces a unique partition of G into disjoint left cosets of the same size. Since this decomposition is always possible, g' (the order of G') must divide g. Therefore, if the order of a group is prime, the group cannot have non-trivial sub-groups. The number of different left cosets $j = g/g'$ is called the *index* j of the sub-group G' relative to G.

In a completely analogous way, one can also construct a division into right cosets R_a. Of relevance in this book is only the case where right and left cosets are identical. We will discuss this situation in the following section.

2.3.5 Normal Sub-groups

A sub-group H of G is said to be *normal* or *invariant sub-group* if and only if its right cosets are identical with its left cosets.

In Abelian groups, every sub-group is obviously a normal sub-group. Every sub-group of index 2 is also a normal sub-group, since there are only two left cosets and two right cosets, one of it being the sub-group itself ($\mathcal{L}_E = \mathcal{R}_E = G'$).

Example As an example of a sub-group that is not normal, we consider the sub-group $G' = \{E, \delta_{21}\}$ of $G = D_3$. Its three left and right cosets are

$$\begin{array}{l|l} \mathcal{L}_E = G' & \mathcal{R}_E = G' \\ \mathcal{L}_{\delta_3} = \mathcal{L}_{\delta_{23}} = \{\delta_3, \delta_{23}\} & \mathcal{R}_{\delta_3} = \mathcal{R}_{\delta_{22}} = \{\delta_3, \delta_{22}\} \\ \mathcal{L}_{\delta_3^2} = \mathcal{L}_{\delta_{22}} = \{\delta_3^2, \delta_{22}\} & \mathcal{R}_{\delta_3^2} = \mathcal{R}_{\delta_{23}} = \{\delta_3^2, \delta_{23}\} \end{array} .$$

Evidently, the left and right cosets are different and G' is therefore not a normal sub-group. In contrast, the sub-group $H = \{E, \delta_3, \delta_3^2\}$ of D_3 has to be normal because it has an index $j = 2$. Its cosets are

$$\begin{aligned} \mathcal{L}_E &= \mathcal{R}_E = H \ , \\ \mathcal{L}_{\delta_{21}} &= \mathcal{R}_{\delta_{21}} = \{\delta_{21}, \delta_{22}, \delta_{23}\} \ . \end{aligned}$$

We can formulate a simple and useful criterion on whether or not a sub-group is normal: H is a normal sub-group of G if and only if H consists of entire classes of G; in other words, if an element of G belongs to H, then the entire class of that element must belong to H.

Proof If

$$H = \{b_1, \ldots, b_m\}$$

consists of entire classes of G and $a \in G$, we find that

$$\mathcal{R}_a = \{b_1 \cdot a, \ldots, b_m \cdot a\} = a \cdot \{a^{-1} \cdot b_1 \cdot a, \ldots, a^{-1} \cdot b_m \cdot a\} \overset{(2.6)}{=} \mathcal{L}_a \ ,$$

and H is a normal sub-group. Conversely, if $\mathcal{R}_a = \mathcal{L}_a \ \forall a$, then $H \cdot a = a \cdot H$ which leads to

$$H = a \cdot H \cdot a^{-1} \ .$$

Since this equation is valid for all a, every class element appears on the right side (for some a) or none. So, the same must be true for the left side, which proves the second direction of the criterion. $\surd$

2.3.6 Factor Groups

If H is a normal sub-group of G, the cosets $\mathcal{L}_a$ can themselves be considered as a group, called the *factor group* G/H, if we define the group algebra as

$$\begin{aligned} \mathcal{L}_a \cdot \mathcal{L}_b &\equiv \mathcal{L}_{a \cdot b} \ , \\ E &\equiv \mathcal{L}_E \ , \\ \mathcal{L}_a^{-1} &\equiv \mathcal{L}_{a^{-1}} \ . \end{aligned}$$

The group properties obviously hold, e.g. the associative law

$$\mathcal{L}_a \cdot (\mathcal{L}_b \cdot \mathcal{L}_c) = \mathcal{L}_a \cdot \mathcal{L}_{b\cdot c} = \mathcal{L}_{a\cdot b\cdot c} = \mathcal{L}_{a\cdot b} \cdot \mathcal{L}_c = (\mathcal{L}_a \cdot \mathcal{L}_b) \cdot \mathcal{L}_c \ . \ \surd$$

It further holds that the elements of $\mathcal{L}_{a\cdot b}$ are all products $a_i \cdot b_j$ of elements $a_i \in \mathcal{L}_a, b_j \in \mathcal{L}_b$. Of course, since $\mathcal{L}_{a\cdot b}$ also has g' elements, each of the $(g')^2$ products $a_i \cdot b_j$ appears in $\mathcal{L}_{a\cdot b}$ only once.

Proof With $a_i \in \mathcal{L}_a$ and $b_j \in \mathcal{L}_b$ we first have to show that $a_i \cdot b_j \in \mathcal{L}_{a\cdot b}$. There exist $h_1, h_2 \in H$ with $a_i = h_1 \cdot a, b_i = b \cdot h_2$. From this, it follows that

$$a_i \cdot b_j = h_1 \cdot a \cdot b \cdot h_2 \ .$$

Since $a \cdot b \cdot h_2 \in \mathcal{L}_{a\cdot b}$ and $\mathcal{R}_{a\cdot b} = \mathcal{L}_{a\cdot b}$ there must be another element $h_2' \in H$ with $a \cdot b \cdot h_2 = h_2' \cdot a \cdot b$. With these we obtain

$$a_i \cdot b_j = \underbrace{h_1 \cdot h_2'}_{\in H} \cdot a \cdot b \quad \Rightarrow a_i \cdot b_j \in \mathcal{L}_{a\cdot b} \ . \ \surd$$

Conversely, let $c \in \mathcal{L}_{a\cdot b}$ be given. Then there exists an $h \in H$ with

$$c = a \cdot \underbrace{b \cdot h}_{\equiv b'} \ ,$$

where $a \in \mathcal{L}_a$ and $b' \in \mathcal{L}_b$, i.e. every element of $\mathcal{L}_{a\cdot b}$ can be written as a product of elements of $\mathcal{L}_a$ and $\mathcal{L}_b$. $\surd$

As an example, we consider again the group D_3. The only non-trivial normal subgroup here is $H = \{E, \delta_3, \delta_3^2\}$. The factor group G/H then has the two elements $\mathcal{L}_E$ and $\mathcal{L}_{\delta_{21}}$ and is isomorphic to C_2.

2.4 Product Groups

For two groups

$$G_1 \equiv \{a_1, a_2, \ldots a_{g_1}\}, \ G_2 \equiv \{b_1, b_2, \ldots b_{g_2}\} \ ,$$

of orders g_1, g_2 one can define the *product group*

$$G \equiv G_1 \times G_2 \ ,$$

with the $g = g_1 \cdot g_2$ elements

$$c_1 \equiv (a_1; b_1), c_2 \equiv (a_1; b_2), \ldots, c_{g_2} \equiv (a_1; b_{g_2}), c_{g_2+1} \equiv (a_2; b_1), \ldots, c_g \equiv (a_{g_1}; b_{g_2}) \ .$$

Table 2.6 Multiplication table of the group $G = C_2 \times C_2$

	$(E_1; E_2)$	$(E_1; a_2)$	$(a_1; E_2)$	$(a_1; a_2)$
$(E_1; E_2)$	$(E_1; E_2)$	$(E_1; a_2)$	$(a_1; E_2)$	$(a_1; a_2)$
$(E_1; a_2)$	$(E_1; a_2)$	$(E_1; E_2)$	$(a_1; a_2)$	$(a_1; E_2)$
$(a_1; E_2)$	$(a_1; E_2)$	$(a_1; a_2)$	$(E_1; E_2)$	$(E_1; a_2)$
$(a_1; a_2)$	$(a_1; a_2)$	$(a_1; E_2)$	$(E_1; a_2)$	$(E_1; E_2)$

With the definition

$$(a_i; b_j) \cdot (a_k; b_l) \equiv (a_i \cdot a_k; b_j \cdot b_l) \ ,$$

of the multiplication in G, the group axioms in Sect. 2.1 are obviously met where

$$c_E \equiv (a_E; b_E) \quad , \quad (a_i; b_j)^{-1} = (a_i^{-1}; b_j^{-1}) \ .$$

Example For example, with Table 2.1 one can derive the multiplication table of the product group $G = C_2 \times C_2$. It is given in Table 2.6. A comparison with Table 2.3 shows that this group is isomorphic to D_2.

Exercises

1. Prove that
   (a) the identity element of a group is unique,
   (b) the inverse element a^{-1} of an element a is unique,
   (c) one could formulate axiom (4) in the definition of groups more weakly: For every element a there is a left inverse a_L^{-1} with $a_L^{-1} \cdot a = E$. Show that one can then conclude: There is also a right inverse a_R^{-1} with $a \cdot a_R^{-1} = E$ and it is $a_R^{-1} = a_L^{-1}$.
2. Verify (2.9).
3. Given a group $G = \{a_1, a_2, \ldots, a_g\}$. The bijective mapping f which assigns to each element of G its inverse, i.e.

$$f(a_i) = a_i^{-1} \ ,$$

   may satisfy

$$f(a_i \cdot a_j) = f(a_i) \cdot f(a_j) \ \ \forall a_i, a_j \in G. \tag{2.15}$$

   Show that G is then Abelian.
4. Consider the group G of the 8 symmetry transformations (rotations and reflections) of a molecule that has the form displayed in Fig. 2.4

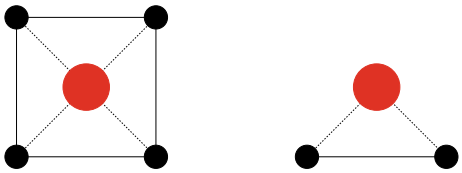

Fig. 2.4 A molecule AB_4 seen from above (left) and from the side (right)

(a) Give all the elements of the group and their inverses and set up the multiplication table.
(b) What sub-groups does G have?
(c) Determine all classes $\mathcal{C}_i$ of G. Calculate for two pairs $\mathcal{C}_1, \mathcal{C}_2$ to be chosen by yourself ($\mathcal{C}_1 \neq \mathcal{C}_2$ and $\mathcal{C}_i \neq \{E\}$) the product of these two classes.
(d) Which of the sub-groups found in b) are normal?

Note: To set up the multiplication table, which is somewhat time-consuming, it makes sense to write a short computer program.

5. We consider the set of 6 matrices

$$\tilde{D}_1 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad , \quad \tilde{D}_2 = \begin{pmatrix} \omega & 0 \\ 0 & \omega^2 \end{pmatrix} \quad , \quad \tilde{D}_3 = \begin{pmatrix} \omega^2 & 0 \\ 0 & \omega \end{pmatrix} \, , \tag{2.16}$$
$$\tilde{D}_4 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad , \quad \tilde{D}_5 = \begin{pmatrix} 0 & \omega \\ \omega^2 & 0 \end{pmatrix} \quad , \quad \tilde{D}_6 = \begin{pmatrix} 0 & \omega^2 \\ \omega & 0 \end{pmatrix} \, ,$$

with $\omega \equiv \exp(2\pi \mathrm{i}/3)$. Show (easiest with the help of a computer) that they form a group. Here, the usual definitions of the multiplication of matrices and the inversion of a matrix are interpreted in the group-theoretic sense. Which of the two groups with 6 elements (see Table 2.2) is it?

6. Show that the following holds for the class multiplication coefficients,

$$f_{ijk} = f_{jik} \, ,$$

even if the group is not Abelian.

7. Show that

(a) the group order is an integer multiple of the order of any element,
(b) all elements of a class have the same order.

8. Show that for the order $g = 4$ there are only the two groups D_2 and C_4 introduced in this chapter.
9. Show that a group whose order is prime must be cyclic. Make use of the fact that such a group can only have trivial sub-groups, as was shown in Sect. 2.3.4. Conversely, show that the order of a group that has only trivial sub-groups must be prime.

10. In the following we consider sets S for which a multiplication operation is defined. Investigate which of the group axioms are fulfilled or can be fulfilled by identifying an identity and an inverse element:

    (a) $S = \mathbb{N}$ with $a \cdot b = \max(a, b)$ for all $a, b \in S$,
    (b) $S = \mathbb{Z}$ with $a \cdot b = a + b + 1$ for all $a, b \in S$,
    (c) $S =$the set of all real invertible matrices with $a \cdot b = ab + ba$ for all $a, b \in S$.

11. The set $P(l)$ of $l!$ permutations can also be viewed as a group. For example, $P(3)$ has the 6 elements

$$P_1[(123)] = (123) \quad , \quad P_2[(123)] = (312) \quad , \quad P_3[(123)] = (231) \quad ,$$
$$P_4[(123)] = (213) \quad , \quad P_5[(123)] = (321) \quad , \quad P_6[(123)] = (132) \quad .$$

    The multiplication of two permutations is then defined as performing the two one after the other, i.e.

$$P_i \cdot P_j[(123)] \equiv P_i[P_j[(123)]] \; .$$

    Determine the multiplication table of this group, maybe with the help of a computer. To which of the two groups with 6 elements is this group isomorphic?

Chapter 3
Point Groups

In this chapter, we introduce *point groups*, which are of great importance in solid-state physics. We start with the general definition of point groups in Sect. 3.1, followed by an exploration of the so-called point groups of the first kind in Sect. 3.2. In Sect. 3.3, we investigate the types of point groups that can occur in solid-state physics before introducing the second kind of point groups in Sect. 3.4. The 32 point groups in solids are then discussed in Sect. 3.5. Finally, in Sect. 3.6, we introduce the notion of *crystal systems*, which allows us to classify Bravais lattices based on their point group symmetries.

3.1 Definition of Point Groups

Our definition of point groups starts from the *orthogonal group* $O(3)$ of all three-dimensional orthogonal matrices $\tilde{O}$, with the defining property

$$\tilde{O}^T \cdot \tilde{O} = \tilde{O} \cdot \tilde{O}^T = \tilde{1} \,. \tag{3.1}$$

The group multiplication here is the ordinary matrix multiplication and it is

$$E = \tilde{1} \,, \;\; \tilde{O}^{-1} = \tilde{O}^T \,.$$

We define *point groups* as all finite sub-groups of $O(3)$. Obviously, $O(3)$ has also infinite sub-groups, e.g. the set of all orthogonal matrices which describe a rotation about a fixed axis (which is, by the way, isomorphic to $O(2)$).

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One distinguishes *point groups of the first kind* (or *proper point groups*) G_p which satisfy[1]

$$|\tilde{O}| = 1 \ \ \forall \ \tilde{O} \in G_\mathrm{p} \ ,$$

from *point groups of the second kind* (or *improper point groups*) G_i where

$$|\tilde{O}| = -1 \ ,$$

for at least one $\tilde{O} \in G_\mathrm{i}$. Elements with $|\tilde{O}| = 1(-1)$ are denoted as proper (improper). We will later show that in improper point groups the number of proper and improper elements must be equal. Improper rotations $\tilde{O}$ can always be written as a product of a proper rotation $\tilde{O}'$ and the inversion matrix

$$\tilde{I} = -\tilde{1} \ ,$$

because the matrix $\tilde{O}' \equiv \tilde{I} \cdot \tilde{O}$ has a determinant $|\tilde{O}'| = 1$ and it is $\tilde{O} = \tilde{I} \cdot \tilde{O}'$ (since $\tilde{I}^2 = E \rightarrow \tilde{I}^{-1} = \tilde{I}$). Whether $\tilde{I}$ and $\tilde{O}'$ are also elements of G_i depends on the improper point group which is considered.

For example, the reflection at the mirror plane $z = 0$, represented by the matrix

$$\tilde{O} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \ ,$$

is an improper group element and is equivalent to a rotation through π about the z-axis (i.e. perpendicular to the mirror plain),

$$\tilde{O}' = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \ ,$$

multiplied with the inversion. The same holds, of course, for any mirror plane.

With our definition so far, the point group of a body or a physical system depends obviously on the choice of the origin of the coordinate system. We always choose the origin which has the largest point group and assume that such an origin exists in an unequivocal way. A proof of this assumption is not necessary, since we will slightly re-define the term 'point group' in Chap. 12 and with that new definition the point group of a solid will be independent of the chosen origin.[2] All statements, however, that we will make in the following about point groups remain valid even with the generalized definition in Chap. 12.

---

[1] Recall that orthogonal matrices $\tilde{O}$ can only have determinants with $|\tilde{O}| = \pm 1$ which follows from (3.1).

[2] Readers interested in space groups can go directly to Chap. 12 after reading this chapter.

3.2 The Point Groups of the First Kind

There exist five types of point groups of the first kind which we shall introduce in the following. A formal proof of this statement may exist in the mathematical literature. In physics, however, we can be satisfied with the fact that no further point groups of the first kind have been found in experiment.

3.2.1 The Groups C_n

The cyclic point group C_n ($n = 2, 3, \ldots$) consists of all n-fold rotations δ_n^m ($m = 0, 1, \ldots, n-1$) about a specific axis. Its n elements can be visualized as rotations that preserve a pyramid above a regular polygon with n vertices, as shown in Fig. 3.1. The group $C_1 = E$, which has only one element, is also considered a member of this family. It should be noted that point groups C_n and C_n', which differ with respect to the rotation axis, are isomorphic.[3]

The sub-groups of C_n are the groups C_l where l is a factor of n. As an Abelian group, all elements of C_n are their own classes.

It is worth noting that here and in the following discussion, we use simple bodies to help with the visualization of the symmetries, even though these bodies actually have a higher symmetry than the one we are considering. For instance, we ignore mirror planes as it has already been the case for the body in Fig. 3.1. However, more complicated bodies with the exact point group symmetry under consideration do

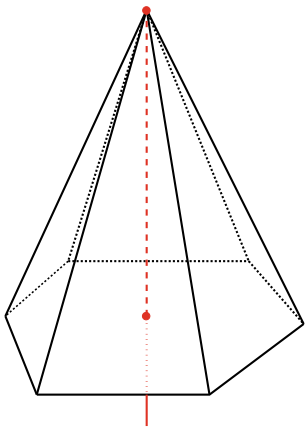

Fig. 3.1 Example of a body which is left unchanged by the elements of a group C_n (here, $n = 6$)

[3] In fact, these groups are not only isomorphic, but also *equivalent*. Two point groups G and G' are said to be equivalent if there exists a non-singular matrix $\tilde{S}$ (i.e. $|\tilde{S}| \neq 0$) such that, for some proper arrangement of the elements, it is $\tilde{O}_i = \tilde{S}\tilde{O}_i'(\tilde{S})^{-1}$, for all $\tilde{O}_i \in G$ (i.e. an *equivalence transformation*). The term 'equivalence' is discussed in detail in Sect. 4.1.

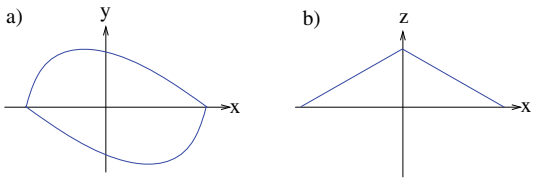

Fig. 3.2 A body with C_2 symmetry viewed from the top (**a**)) and from one side (**b**))

always exist. For example, the body depicted in Fig. 3.2 has the point group C_2 and no further symmetries.

3.2.2 The Groups D_n

The groups known as *dihedral groups* and denoted as D_n ($n = 2, 3, \ldots$), are obtained by augmenting the groups C_n with n two-fold rotation axes perpendicular to the main axis of rotation. The groups have $2n$ elements that can be interpreted as rotations preserving a prism situated over a regular polygon with n vertices, as depicted in Fig. 3.3. As previously seen in the case of the group D_3, the dihedral groups D_n can be non-Abelian (see Sect. 2.2.3). Figure 3.3 shows that the situation is different for odd and even values of n. For even n, the two-fold symmetry axes connect opposite faces or edges of the prism, while in odd cases, they connect opposite edges and faces. This difference between odd and even n is also reflected in the class and sub-group structure:

even n:
The sub-groups of D_n are D_l and C_l with l being a factor of n. With $m \equiv n/2 \in \mathbb{N}$ one finds that the group D_n consists of the following $r = m + 3$ classes

$$D_{2m} = \{E\} \cup \underbrace{\{\delta_n^m\}}_{180^\circ} \cup \underbrace{\{\delta_n^{m'}, (\delta_n^{m'})^{-1}\}}_{1 \le m' < m} \cup \{\delta_{2,1}, \delta_{2,3}, \ldots\} \cup \{\delta_{2,2}, \delta_{2,4}, \ldots\} \,.$$

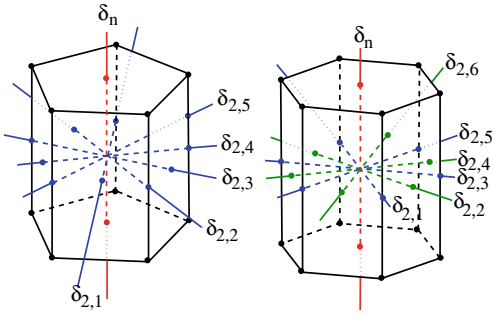

Fig. 3.3 Examples of bodies which are left unchanged by the elements of a group D_n (here, $n = 5$ left, and $n = 6$ right); red: the n-fold symmetry axis, blue and green: the two-fold symmetry axes

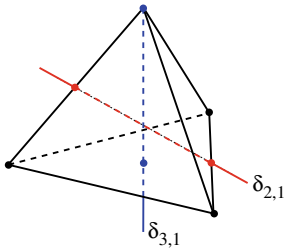

Fig. 3.4 2 of the 7 rotational axes that leave a regular tetrahedron unchanged

odd n:
The sub-groups of D_n are the same as for even n plus C_2 because this group is not included in the sub-groups of the main rotation axis. With $m \equiv (n-1)/2 \in \mathbb{N}$ one finds the following $r = m + 2$ classes

$$D_{2m+1} = \{E\} \cup \underbrace{\{\delta_n^{m'}, (\delta_n^{m'})^{-1}\}}_{1 \le m' \le m} \cup \{\delta_{2,1}, \delta_{2,2}, \dots\} \; .$$

3.2.3 The Tetrahedral Group T

The *tetrahedral group T* consists of all rotations which leave unchanged a regular tetrahedron. These are (see Fig. 3.4),

(i) three two-fold axes $\delta_{2,i}$ $(i = 1, 2, 3)$ through the centers of opposite edges,
(ii) four three-fold axes $\delta_{3,i}$ $(i = 1, \dots 4)$ through the vertex corners and the opposite faces.

The group has 12 elements, three sub-groups, D_2, C_3, and C_2 (and their sub-groups) and consists of $r = 4$ classes,

$$T = \{E\} \cup \{3\delta_{2,i}\} \cup \{4\delta_{3,i}\} \cup \{4\delta_{3,i}^2\} \; .$$

3.2.4 The Cubic Group O

The *cubic group O* consists of all rotations that leave a cube unchanged. These rotations are (see Fig. 3.5):

(i) six two-fold axes $\delta_{2,i}$ $(i = 1, \dots, 6)$ passing through the centers of opposite edges,
(ii) four three-fold axes $\delta_{3,i}$ $(i = 1, \dots 4)$ passing through opposite vertex corners, and

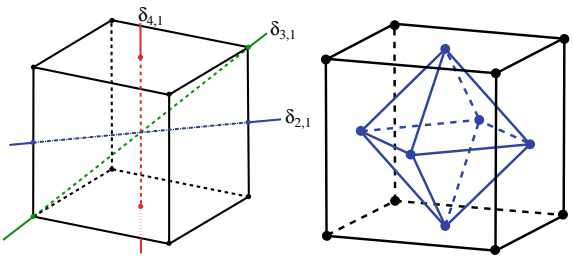

Fig. 3.5 Left: 3 of the 13 rotational axes that leave a cube unchanged; right: the centers of a cube's faces form a regular octahedron

(iii) three four-fold axes $\delta_{4,i}$ $(i = 1, 2, 3)$ passing through the centers of opposite faces.

The group has a total of 24 elements. Its sub-groups include T, D_4, D_3, and their respective sub-groups. The class structure of the group is $(r = 5)$,

$$O = \{E\} \cup \{3\delta_{4,i}, 3\delta_{4,i}^3\} \cup \{3\delta_{4,i}^2\} \cup \{6\delta_{2,i}\} \cup \{4\delta_{3,i}, 4\delta_{3,i}^2\} \ .$$

The group O is isomorphic (and even equivalent[4]) to the symmetry group of a regular octahedron. This can be seen in Fig. 3.5, where it becomes evident that the centers of the faces of a cube are the vertices of a regular octahedron.

3.2.5 *Icosahedron Group Y*

The final point group of the first kind is the *Icosahedron Group Y*, which comprises all rotations that leave a regular icosahedron unchanged. An icosahedron is a body with 20 equilateral triangles as faces, as shown in Fig. 3.6 (left). The 120 elements of Y consist of:

(i) 15 two-fold axes $\delta_{2,i}$ $(i = 1, \ldots, 15)$ through the centers of opposite edges.
(ii) 10 three-fold axes $\delta_{3,i}$ $(i = 1, \ldots 4)$ through opposite vertex corners and faces.
(iii) Three four-fold axes $\delta_{4,i}$ $(i = 1, 2, 3)$ through the centers of opposite faces.

The group Y is isomorphic to the symmetry group of a dodecahedron, as depicted in Fig. 3.6 (right). However, the icosahedron group does not occur in solids, as we will demonstrate in the next section, so we will not elaborate on it further here.

[4] See Footnote 2.

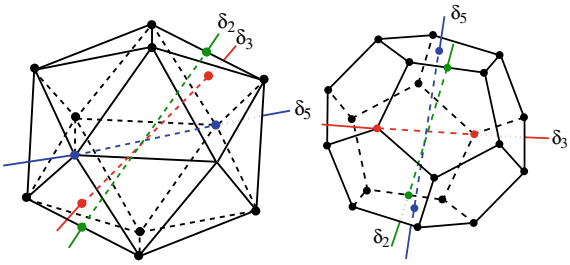

Fig. 3.6 Left: icosahedron; right: dodecahedron

3.3 Point Groups in Solids

Before we discuss the point groups of the 2nd kind, we want to prove an important theorem: In crystalline solids, n-fold rotations can be symmetry transformations only if $n = 2, 3, 4,$ or 6.

Proof A crystal is characterized by a Bravais lattice, which is defined by the basis vectors $\vec{b}_i$, and a basis of vectors $\vec{R}_i$ that belong to each Bravais lattice point. Figure 3.7 shows a two-dimensional example. An orthogonal matrix $\tilde{O}$ that preserves a crystal lattice must also preserve the underlying Bravais lattice. Therefore, we can restrict our discussion to Bravais lattices. The sites of such a lattice are described by

$$\vec{B}(n_1, n_2, n_3) = \sum_{i=1}^{3} n_i \cdot \vec{b}_i \ , \tag{3.2}$$

where $n_i \in \mathbb{Z}$. By a proper choice of the Euclidean basis vectors $\vec{e}_i$ a rotation can always be represented by a matrix of the form (see Exercise 3 in Chap. 1)

$$\tilde{O} = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \ . \tag{3.3}$$

Let $\tilde{U}$ be the matrix that connects the two basis sets, i.e.

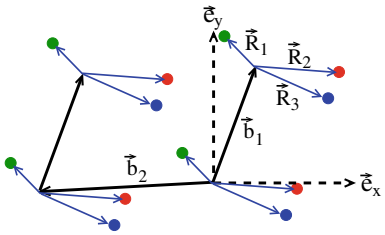

Fig. 3.7 Example of a Bravais lattice in 2 dimensions. The Bravais lattice is defined by the vectors $\vec{b}_i$. The vectors $\vec{R}_i$ define a basis at each Bravais lattice site.

$$\vec{b}_i = \sum_j U_{j,i} \cdot \vec{e}_j \ .$$

Then the matrix representation $\tilde{O}'$ of the rotation in the basis $\vec{b}_i$,

$$\tilde{O} \cdot \vec{b}_i = \sum_j O'_{j,i} \cdot \vec{b}_j \ ,$$

is given by[5]

$$\tilde{O}' = \tilde{U}^{-1} \cdot \tilde{O} \cdot \tilde{U} \ . \tag{3.4}$$

If $\tilde{O}$ is a symmetry transformation, then $\tilde{O}$, applied to a Bravais lattice vector (3.2), must yield another such vector,

$$\tilde{O} \cdot \vec{B} = \sum_i n_i \cdot \tilde{O} \cdot \vec{b}_i = \sum_{i,j} n_i \cdot O'_{j,i} \cdot \vec{b}_j \stackrel{!}{=} \sum_j n'_j \cdot \vec{b}_j \ .$$

The resulting equation

$$\sum_i O'_{j,i} \cdot n_i = n'_j \in \mathbb{Z} \ ,$$

must be fulfilled for all (integer) values of n_i which is only possible if $O'_{j,i} \in \mathbb{Z}$, $\forall i, j$. Then the trace of the matrix (3.4) must be integer too,

$$\mathrm{tr}(\tilde{O}') = \mathrm{tr}(\tilde{U}^{-1} \cdot \tilde{O} \cdot \tilde{U}) = \mathrm{tr}(\tilde{O}) = 2\cos\alpha + 1 \equiv T(\alpha) \in \mathbb{Z} \ , \tag{3.5}$$

where we have used the invariance of the trace under cyclic permutations. As one can see in Fig. 3.8, the function $T(\alpha)$ is integer only for the following angles

$$\frac{\alpha}{2\pi} = \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \frac{1}{6} \ , \tag{3.6}$$

and multiples of these.

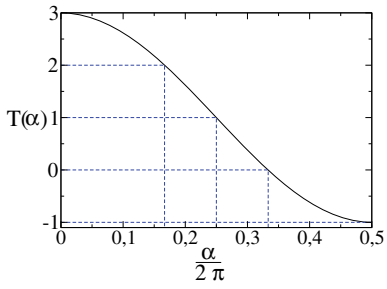

Fig. 3.8 Solid line: the function (3.5); dashed lines: the points where the function takes integer values

[5] This equation is shown in every text book on linear algebra.

With (3.6) we have established the necessary criterion to determine possible rotational symmetries in solids. Later on, we will see that all of these rotational symmetries do indeed occur in some lattices. The point groups of the first kind that satisfy (3.6) are listed as follows:

$$C_1, C_2, C_3, C_4, D_2, C_6, D_3, D_4, D_6, T, O \ . \tag{3.7}$$

It was previously shown in Sect. 3.1 that any improper rotation can be expressed as a product of a proper rotation and the inversion. Since the inversion is always a symmetry of a Bravais lattice, the angles (3.6) are also the only possible ones that can occur in the rotational part of improper rotational symmetries in solids.

3.4 The Point Groups of the Second Kind

If G is an improper point group, then its sub-group G_0 consisting of proper rotations is a normal sub-group of G with index 2. This means that there exist two cosets, G_0 and L_0, where L_0 contains all the improper rotations.

Proof Demonstrating that G_0 and L_0 have equal numbers of elements would be sufficient to establish their index as $j = g/g_0 = 2$. Since E is always an element of G_0, the latter cannot be empty. Let $\tilde{O}$ be an element of L_0. Then, we have

$$\{\underbrace{\tilde{O} \cdot G_0}_{=L_0}, \underbrace{\tilde{O} \cdot L_0}_{=G_0}\} \overset{(2.4)}{=} G \ ,$$

because the elements $\tilde{O} \cdot G_0$ and $\tilde{O} \cdot L_0$ have determinants 1 and -1 respectively. This proves the above statement. $\surd$

It should be noted that the inversion itself may not be a member of L_0. For instance, in a tetrahedron, there are mirror planes in addition to the rotational axes, but the inversion is not a symmetry operation. In the following sections, we will examine improper point groups that either include or exclude the inversion.

3.4.1 Improper Point Groups Without the Inversion

As we will demonstrate now, improper point groups that do not include the inversion are isomorphic to one of the proper point groups already introduced in Sect. 3.2, making them mathematically identical. In Sect. 3.5, however, we will provide physical justifications why it is still meaningful to introduce these groups and to distinguish them from their proper counterparts.

Proof We decompose the improper point group (as above),

$$G = \{G_0, L_0\} ,$$

and define

$$L_0' \equiv \tilde{I} \cdot L_0 . \tag{3.8}$$

We will now give the proof of the above statement in three steps:

(i) L_0' is (obviously) a set of proper rotations, of which none is in G_0. We can show this as follows: With $\tilde{O} \in L_0'$ it is $\tilde{I} \cdot \tilde{O} \in G$ (since $\tilde{I}^2 = \tilde{1}$). If $\tilde{O}$ were also in G_0 (and therefore also in G), then also

$$\tilde{I} \cdot \tilde{O} \cdot \tilde{O}^{-1} = \tilde{I} \in G ,$$

contrary to the assumption. $\surd$

(ii) All elements of L_0' are point group operations of a lattice, since every $\tilde{O} \in L_0$ leaves some Bravais lattice invariant by assumption. This also means that $\tilde{I} \cdot \tilde{O} \in L_0'$ (as $\tilde{I}$ is a symmetry of all Bravais lattices). Hence, all elements of L_0' satisfy (3.6).

(iii) Finally, the proper point group $G' \equiv \{G_0, L_0'\}$ is isomorphic to G which follows from the simple bijective mapping $f : G \leftrightarrow G'$:

$$\begin{aligned} a \in G_0 &\rightarrow f(a) = a \in G' , \\ a \in L_0 &\rightarrow f(a) = I \cdot a \in G' . \end{aligned}$$

This mapping fulfills condition (2.1) because $\tilde{I}$ commutes with all point group elements. $\surd$

Example As an example, we consider a pyramid over a rectangle. The proper point group of this body is $G_0 = C_2 = \{E, \delta_{2z}\}$, where the symmetry axis is $\vec{e}_z$. In addition, there are two improper symmetry transformations, namely the mirror planes σ_x $(x = 0)$ and σ_y $(y = 0)$. These two planes form the coset of G_0, denoted as $L_0 = \{\sigma_x, \sigma_y\}$. Together, G_0 and L_0 form the group.

$$C_{2v} \equiv \{E, \delta_{2z}, \sigma_x, \sigma_y\} .$$

Given the previous analysis, we know that C_{2v} is isomorphic to a proper point group. Furthermore, we have found the technique to create the latter. Equation (3.8) implies that we simply need to multiply $\tilde{I}$ with L_0 to obtain the proper point group,

$$L_0' = \{\tilde{I}\sigma_x, \tilde{I}\sigma_y\} = \{\delta_{2,y}, \delta_{2,x}\} .$$

where $\delta_{2,x}$, $\delta_{2,y}$ are two-fold rotations about the $x-$ and $y-$axis. When combined with $G_0 = C_2$, we obtain the proper point group D_2. Using a similar approach, we

Table 3.1 The improper point groups $G = \{G_0, L_0\}$ in solids that do not contain the inversion. The symbols used in this table are introduced in Appendix A where we discuss the Frobenius and the international notation

G_0	G	Elements of L_0
C_1	C_s	σ
C_2	S_4	σ_4, σ_4^3
C_2	C_{2v}	2σ
C_3	C_{3h}	$\sigma_3, \sigma_3^3(=\sigma), \sigma_3^5$
C_3	C_{3v}	3σ
C_4	C_{4v}	4σ
D_2	D_{2d}	$\sigma_4, \sigma_4^3, 2\sigma$
C_6	C_{6v}	6σ
D_3	D_{3h}	$\sigma_3, \sigma_3^3(=\sigma), \sigma_3^5, 3\sigma$
T	T_d	$6\sigma, 3\sigma_4, 3\sigma_4^3$

can obtain the relevant point groups of the second type by including specific improper symmetries to the point groups of the first type. Table 3.1 displays the proper point groups G_0 of order g and their corresponding improper point groups $G = \{G_0, L_0\}$ of order $2g$, with G_0 serving as the normal sub-group.

3.4.2 Improper Point Groups which Include the Inversion

Setting up the improper point groups that do contain the inversion is even easier than those that do not, because they have the simple product form

$$G = G_0 \times (\tilde{1}, \tilde{I}) = \{G_0, \tilde{I} \cdot G_0\} ,$$

where G_0 is one of the 11 proper point groups. Four of these improper point groups are again isomorphic to one of the proper ones, namely

$$C_1 \times (\tilde{1}, \tilde{I}) \widehat{=} C_2 , \; C_2 \times (\tilde{1}, \tilde{I}) \widehat{=} D_2 , \; C_3 \times (\tilde{1}, \tilde{I}) \widehat{=} C_6 , \; D_3 \times (\tilde{1}, \tilde{I}) \widehat{=} D_6 .$$

As a result, we can tentatively state that precisely 18 distinct point groups, referred to as *abstract point groups*, can be realized in solids. However, it will become clear in the next section and in later chapters that the lack of isomorphism is not the appropriate mean to distinguish point groups from each other in physics.

3.5 The 32 Point Groups in Solids

By asserting that there are 18 different point groups in solids, we mean that they are not isomorphic. It is crucial to note that two point groups that are identical in the abstract sense may not be equivalent.[6] For example, we may consider the two groups from Sect. 3.4.1,

$$C_{2v} = \left\{ \tilde{E}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right\} , \tag{3.9}$$

$$D_2 = \left\{ \tilde{E}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right\} .$$

These two collections of matrices cannot be converted into one another via an *equivalence transformation*. This can already be discerned from the fact that the traces of these matrices differ, and the trace is invariant under an equivalence transformation.

In later chapters (e.g. Chap. 9), we will see that two physical systems with isomorphic but inequivalent point groups can have vastly distinct properties. Therefore, in physics, the concept of equivalence of point groups is more relevant than that of isomorphism.[7] In total, there are 32 *inequivalent* point groups in solids, as listed in Table 3.2. All groups in a row of that table are isomorphic to the same abstract point group specified in the first column. The two notations, e.g. C_{2h} and $\left[\frac{2}{m}\right]$, are explained in Appendix A.2.

The sub-group tree depicted in Fig. 3.9 makes it simple to identify the sub-groups of all 32 groups.

3.6 The Seven Crystal Systems

We want to examine which of the 32 point groups can be realized in a Bravais lattice. It is evident that not all 32 can be realized since, e.g. the inversion must always be included in such a point group. As a result, this excludes all groups in the 3rd and 5th columns of Table 3.2.

In fact, there are only seven point groups that can be realized in Bravais lattices. They are denoted as *crystal systems* and are listed in Table 3.3. The table also indicates which point groups can be realized when there is a basis with more than one atom per Bravais lattice site.

In Fig. 3.1, point groups that crystallize in the same Bravais lattice are highlighted with the same color. However, the question of why, for example, a basis with C_1

[6] See Footnote 2.

[7] Conversely, equivalent point groups are isomorphic, as the reader may verify in Exercise 8.

Table 3.2 The 32 inequivalent point groups in solids

Order	Abstract point group	Point groups of the 1. kind	Point groups of the 2. kind with I	Point groups of the 2. kind without I
1	C_1	C_1 [1]		
2	C_2	C_2 [2]	C_i [$\bar{1}$]	C_s
3	C_3	C_3 [3]		
4	C_4	C_4 [4]		S_4 [$\bar{4}$]
4	D_2	D_2 [222]	C_{2h} $\left[\frac{2}{m}\right]$	C_{2v} $\left[2\frac{2}{m}\frac{2}{m}\right]$
6	C_6	C_6 [6]	S_6 [$\bar{3}$]	C_{3h} $\bar{6}$
6	D_3	D_3 [32]		C_{3v} $\left[3\frac{2}{m}\right]$
8	D_4	D_4 [422]		C_{4v} $\left[4\frac{2}{m}\frac{2}{m}\right]$, D_{2d} $\left[\bar{4}2\frac{2}{m}\right]$
8	$C_4 \times C_2$		C_{4h} $\left[\frac{4}{m}\right]$	
8	$D_2 \times C_2$		D_{2h} $\left[\frac{2}{m}\frac{2}{m}\frac{2}{m}\right]$	
12	D_6	D_6 [622]	D_{3d} $\left[\bar{3}\frac{2}{m}\right]$	C_{6v} $\left[6\frac{2}{m}\frac{2}{m}\right]$, D_{3h} $\left[\bar{6}\frac{2}{m}2\right]$
12	T	T [23]		
12	$C_6 \times C_2$		C_{6h} $\left[\frac{6}{m}\right]$	
16	$D_4 \times C_2$		D_{4h} $\left[\frac{4}{m}\frac{2}{m}\frac{2}{m}\right]$	
24	O	O [432]		T_d $\left[\bar{4}3\frac{2}{m}\right]$
24	$D_6 \times C_2$		D_{6h} $\left[\frac{6}{m}\frac{2}{m}\frac{2}{m}\right]$	
24	$T \times C_2$		T_h $\left[\frac{2}{m}\bar{3}\right]$	
48	$O \times C_2$		O_h $\left[\frac{4}{m}\bar{3}\frac{2}{m}\right]$	

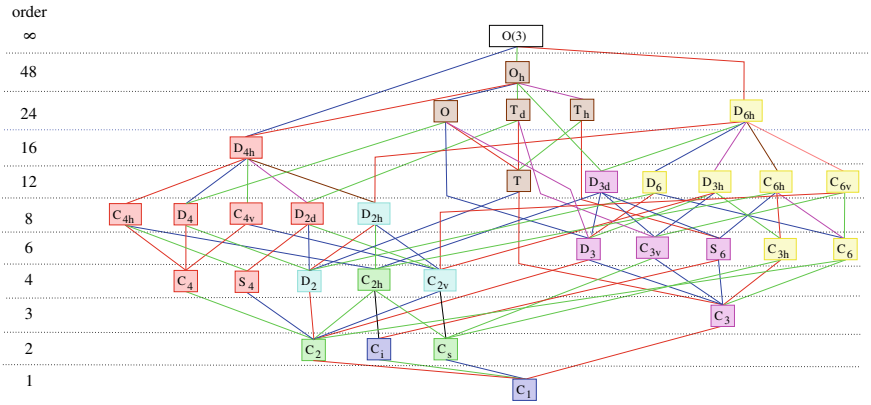

Fig. 3.9 The sub-group relationships of the 32 point groups in solids

Table 3.3 The 7 crystal systems, the corresponding point group, possible point groups when there is a basis of more than one atom per Bravais lattice site

#	Crystal system	Point group	Possible point groups
1.	Triclinic	C_i	C_1
2.	Monoclinic	C_{2h}	C_2, C_s
3.	Orthorhombic	D_{2h}	C_{2v}, D_2
4.	Rhombohedral	D_{3d}	C_3, S_6, D_3, C_{3v}
5.	Tetragonal	D_{4h}	$C_4, S_4, C_{4h}, D_4, C_{4v}, D_{2d}$
6.	Hexagonal	D_{6h}	$C_6, C_{3h}, C_{6h}, D_6, C_{6v}, D_{3h}$
7.	Cubic	O_h	T, T_h, T_d, O, O_h

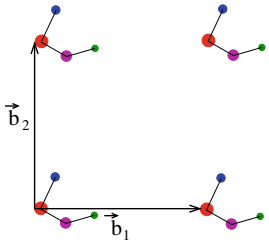

Fig. 3.10 An artificial molecule on a square lattice

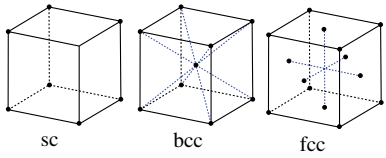

Fig. 3.11 Simple, body-centered, and face-centered cubic lattices

symmetry cannot exist in a cubic lattice can only be answered with physical, rather than mathematical, arguments. For instance, Fig. 3.10 shows that a two-dimensional molecule with a C_1 point group symmetry could, in theory, be placed on a square lattice. Mathematically, this is not impossible, but in physics, such a situation is unlikely because the interaction of the molecules would distort the square lattice. Thus, the fourth column in Table 3.3 represents an experimental finding rather than a mathematical statement that could be derived from group theory.

In introductory lectures on solid-state physics, typically 14 distinct Bravais lattices are introduced, including simple (sc), body-centered (bcc), and face-centered (fcc) cubic lattices as shown in Fig. 3.11. Although the point group of all three lattices is O_h, distinguishing them from each other in group-theoretical terms requires the consideration of space groups that incorporate not only rotational symmetries, but also translational symmetry. These will be discussed in Chap. 12.[8]

[8] See Footnote 2.

Exercises

1. Verify the class division of the group D_3 claimed in Sect. 3.2 using the multiplication Table 2.5.
2. We consider the molecule shown in Fig. 3.13 which has a point group G with 8 elements.

   (a) List all the elements of G along with their inverses and construct the multiplication table. Determine the international notation of this group.
   (b) Find a normal sub-group H of G with 2 elements. Give the corresponding cosets and determine the group table of the factor group G/H.

   Hint: The point group G has three two-fold axes of rotation, two of which one may not see immediately. To construct the multiplication table, which can be quite time-consuming, it may again be helpful to write a computer program.
3. Consider a solid with (identical) atoms on a simple cubic lattice. Into this solid we bring another atom on

   (a) an edge,
   (b) a surface diagonal,
   (c) a space diagonal,

   of a cubic unit cell, see Fig. 3.12. Determine in all three cases the proper and the full point group at the site of the atom.

   Note: In all three cases one has to distinguish between the respective points in the middle and all other points. In your considerations, you should assume that the position of the other atoms remains unchanged, i.e. they simply generate a (constant) potential for the additional atom.
4. What point group does a body have that is infinitely extended in one spatial direction and has the shape of a

   (i) square,
   (ii) rectangle,

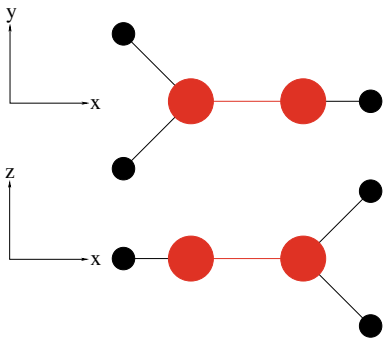

Fig. 3.12 Cubic unit cell and the three lines (in green and dashed) on which the additional atom is brought

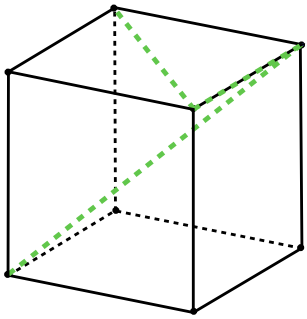

Fig. 3.13 A molecule viewed along the z-axis (top) and the the y-axis (bottom)

(iii) equilateral triangle,
(iv) isosceles triangle,

in the plane perpendicular to it?

5. Create molecules which have the (maximum) symmetry groups

(i) D_2,
(ii) D_{3h}.

There is obviously an infinite number of solutions here.

6. Which of the 32 point groups can be found in every effectively two-dimensional system in solids?
7. Suppose an atom is situated at the center of a cubic box, such that its symmetry group is O_h. How does the symmetry group change when the cube is stretched symmetrically along one of its diagonals?
8. Show that two equivalent point groups are isomorphic.
9. Is the product group $C_2 \times C_4$ isomorphic to C_8?

Chapter 4
Representations and Characters

In this chapter, we delve into the central concept of group theory: the representation of finite groups, with a particular focus on irreducible representations. The notion of representation is closely related to that of matrix groups, which we introduce first in Sect. 4.1. In Sect. 4.2, we explore representations in detail and discuss their most important properties.

4.1 Matrix Groups

A *matrix group* of order g and dimension d is a set of g quadratic (generally complex) matrices of dimension d,

$$\bar{D} \equiv \{\tilde{D}_1, \ldots, \tilde{D}_g\} \ ,$$

that satisfy the group axioms with the group multiplication defined as the ordinary matrix multiplication. It is important to note that all matrices in a matrix group must be non-singular ($|\tilde{D}_i| \neq 0$) since the inverse matrix must also exist and be an element of the group. The matrix $\tilde{1}$ of dimension d must also be an element of the group as the identity element. For instance, the matrices (2.16) with $g = 6$ form a group, as shown in Exercise 5 of Chap. 2. Since this group is non-Abelian, it must be isomorphic to D_3, according to Table 2.2 and the considerations on that table.

4.1.1 Equivalent and Irreducible Matrix Groups

Two matrix groups $\bar{D}$, $\bar{D}'$ of the same order and dimension are called *equivalent* ($\bar{D} \sim \bar{D}'$) if there is a non-singular matrix $\tilde{S}$ ($|\tilde{S}| \neq 0$) such that

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J. Bünemann, *Group Theory in Physics*, Undergraduate Lecture Notes in Physics,
https://doi.org/10.1007/978-3-031-55268-7_4

$$\tilde{D}_i' = \tilde{S}^{-1} \cdot \tilde{D}_i \cdot \tilde{S} \ \ \forall i \qquad \text{or in short:} \qquad \bar{D}' = \bar{S}^{-1} \cdot \bar{D} \cdot \bar{S} \ .$$

The matrix $\tilde{S}$ must be the **same** for all $\tilde{D}_i$. When $g = 1$, this definition corresponds to the equivalence of matrices in linear algebra.

We will use the following mathematical theorem several times in this book: Every finite matrix group is equivalent to a unitary matrix group, i.e. a matrix group comprising solely unitary matrices.

Proof Let $\bar{D} = \{\tilde{D}_1, \ldots, \tilde{D}_g\}$ be a matrix group of dimension d. Then, we define the matrix

$$\tilde{H} \equiv \sum_{i=1}^{g} \tilde{D}_i \cdot \tilde{D}_i^\dagger \ , \tag{4.1}$$

which is Hermitian and positive definite. The hermiticity is obvious and with an arbitrary vector $\vec{v} \in \mathbb{C}^d$ we find

$$\vec{v}^\dagger \cdot \tilde{H} \cdot \vec{v} = \sum_{i=1}^{g} \underbrace{\vec{v}^\dagger \cdot \tilde{D}_i}_{(\tilde{D}_i^\dagger \cdot \vec{v})^\dagger} \cdot \tilde{D}_i^\dagger \cdot \vec{v} = \sum_{i=1}^{g} \underbrace{|\tilde{D}_i^\dagger \cdot \vec{v}|^2}_{\geq 0} \geq 0 \ ,$$

which proves that $\hat{H}$ is positive definite. Let $\tilde{H}$ be diagonalized by the unitary matrix $\tilde{U}$,

$$\tilde{U}^\dagger \cdot \tilde{H} \cdot \tilde{U} = \tilde{A} \equiv \begin{pmatrix} a_1 & & 0 \\ & \ddots & \\ 0 & & a_d \end{pmatrix} \ . \tag{4.2}$$

Since $\tilde{H}$ is positive definite we have eigenvalues $a_i \geq 0$. The following matrix is therefore well defined

$$\sqrt{\tilde{A}} \equiv \begin{pmatrix} \sqrt{a_1} & & 0 \\ & \ddots & \\ 0 & & \sqrt{a_d} \end{pmatrix} \ ,$$

and can be used to define the transformation matrix $\tilde{S} \equiv \tilde{U} \cdot \sqrt{\tilde{A}}$ for which holds

$$\tilde{S} \cdot \tilde{S}^\dagger = \tilde{U} \cdot \tilde{A} \cdot \tilde{U}^\dagger \overset{(4.2)}{=} \tilde{H} \ . \tag{4.3}$$

As the last step of the proof, we have to show that the transformed matrices

$$\tilde{D}_i' \equiv \tilde{S}^{-1} \cdot \tilde{D}_i \cdot \tilde{S} \ , \tag{4.4}$$

are unitary,

$$\begin{aligned}
\tilde{D}'_i \cdot \left(\tilde{D}'_i\right)^\dagger &\overset{(4.4)}{=} \tilde{S}^{-1} \cdot \tilde{D}_i \cdot \tilde{S} \cdot \left(\tilde{S}^{-1} \cdot \tilde{D}_i \cdot \tilde{S}\right)^\dagger \\
&= \tilde{S}^{-1} \cdot \tilde{D}_i \cdot \tilde{S} \cdot \tilde{S}^\dagger \cdot \tilde{D}_i^\dagger \cdot \underbrace{\left(\tilde{S}^{-1}\right)^\dagger}_{=\left(\tilde{S}^\dagger\right)^{-1}} \\
&\overset{(4.3)}{=} \tilde{S}^{-1} \cdot \tilde{D}_i \cdot \tilde{H} \cdot \tilde{D}_i^\dagger \cdot \left(\tilde{S}^\dagger\right)^{-1} \\
&\overset{(4.1)}{=} \sum_j \tilde{S}^{-1} \cdot \tilde{D}_i \cdot \tilde{D}_j \cdot (\tilde{D}_i \cdot \tilde{D}_j)^\dagger \cdot \left(\tilde{S}^\dagger\right)^{-1} .
\end{aligned}$$

Note that, up to this point, we have not yet used the fact that the matrices $\tilde{D}_i$ form a group. With the rearrangement theorem (2.4), we can replace the sum over $\tilde{D}_i \cdot \tilde{D}_j$ by a sum over $\tilde{D}_j$ to obtain

$$\begin{aligned}
\tilde{D}'_i \cdot \left(\tilde{D}'_i\right)^\dagger &= \sum_j \tilde{S}^{-1} \cdot \tilde{D}_j \cdot (\tilde{D}_j)^\dagger \cdot \left(\tilde{S}^\dagger\right)^{-1} \\
&\overset{(4.1)}{=} \tilde{S}^{-1} \cdot \tilde{H} \cdot \left(\tilde{S}^\dagger\right)^{-1} \overset{(4.3)}{=} \tilde{1} . \quad \surd
\end{aligned}$$

Suppose $\bar{D}$ and $\bar{D}'$ are matrix groups with the same order g but with not necessarily identical dimensions d and d'. The direct sum $\bar{D} \oplus \bar{D}'$ of the matrix groups is then defined as

$$\bar{D} \oplus \bar{D}' \equiv \{\tilde{D}_1 \oplus \tilde{D}'_1, \ldots, \tilde{D}_g \oplus \tilde{D}'_g\} ,$$

with the $(d + d')$-dimensional matrices

$$\tilde{D}_i \oplus \tilde{D}'_i \equiv \begin{pmatrix} \tilde{D}_i & \tilde{0} \\ \tilde{0} & \tilde{D}'_i \end{pmatrix} .$$

Such matrix groups are called *block diagonal*.

A matrix group $\bar{D}$ is denoted as *reducible* if it is equivalent to a direct sum of two matrix groups $\bar{D}^{(1)}$, $\bar{D}^{(2)}$ of smaller dimensions. This means that there is a matrix $\tilde{S}$ such that

$$\tilde{S}^{-1} \cdot \bar{D} \cdot \tilde{S} = \{\tilde{S}^{-1} \cdot \tilde{D}_1 \cdot \tilde{S}, \ldots, \tilde{S}^{-1} \cdot \tilde{D}_g \cdot \tilde{S}\} = \bar{D}^{(1)} \oplus \bar{D}^{(2)} .$$

Otherwise $\bar{D}$ is denoted as *irreducible*.

The following rule applies: If the matrix groups $\bar{D}$ and $\bar{D}'$ are equivalent, i.e. there is a matrix $\tilde{S}$ with

$$\bar{D}' = \tilde{S}^{-1} \cdot \bar{D} \cdot \tilde{S} , \tag{4.5}$$

then either both are reducible or both are irreducible.

Proof Assume that $\bar{D}$ is irreducible and $\tilde{P}^{-1} \cdot \bar{D}' \cdot \tilde{P}$ is block diagonal (i.e. $\bar{D}'$ is reducible). Then we find with (4.5) that

$$\underbrace{\tilde{P}^{-1} \cdot \tilde{S}^{-1}}_{\equiv \tilde{R}^{-1}} \cdot \bar{D} \cdot \underbrace{\tilde{P} \cdot \tilde{S}}_{\equiv \tilde{R}} ,$$

is also block diagonal, contrary to the assumption. $\surd$

4.1.2 Schur's Lemma

Both versions of Schur's lemma make mathematical statements that have no particular significance in most parts of this book. The lemma is only needed in central proofs in Chap. 5 and there seems to be a consensus in the literature that it is indispensable for these proofs. Readers who are not interested in all details of proofs can safely skip this section.

To prove Schur's lemma below, we first need the following fact: Let $\bar{D}$ be a matrix group of dimension d. Then, obviously, every element $\tilde{D}_i \in \bar{D}$ is a linear map in the vector space $\underline{V}^d \equiv \mathbb{C}^d$. If $\bar{D}$ is irreducible, then there is no non-trivial subspace $\underline{V}^{d'}$ of $\underline{V}^d$ that is invariant under all $\tilde{D}_i$.[1] Invariance in this context means that

$$\vec{v} \in \underline{V}^{d'} \implies \tilde{D}_i \cdot \vec{v} \in \underline{V}^{d'} .$$

Proof We give the proof in two steps.

(i) Let

$$\bar{D}' = \hat{S}^{-1} \cdot \bar{D} \cdot \hat{S} , \tag{4.6}$$

be a unitary matrix group equivalent to $\bar{D}$ (which exists as shown in Sect. 4.1.1). If $\bar{D}'$ has an invariant subspace $\underline{V}^{d'}$, so does $\bar{D}$ (and vice versa), namely

$$\underline{U}^{d'} \equiv \hat{S} \cdot \underline{V}^{d'} . \tag{4.7}$$

The two sub spaces $\underline{V}^{d'}$, $\underline{U}^{d'}$ have the same dimension since $|\hat{S}| \neq 0$. That $\underline{U}^{d'}$ is an invariant subspace of $\bar{D}$ follows from

$$\tilde{D}_i \cdot \underline{U}^{d'} \overset{(4.7)}{=} \tilde{D}_i \cdot \tilde{S} \cdot \underline{V}^{d'} \overset{(4.6)}{=} \hat{S} \cdot \tilde{D}'_i \cdot \tilde{S}^{-1} \tilde{S} \cdot \underline{V}^{d'} = \tilde{S} \cdot \underbrace{\tilde{D}'_i \cdot \underline{V}^{d'}}_{\in \underline{V}^{d'}} \in \underline{U}^{d'} . \surd$$

Given this result, we can proceed with the second step of the proof assuming that $\bar{D}$ forms a unitary matrix group.

[1] Here, *non-trivial* means $d' \neq 0$ and $d' \neq d$.

(ii) Let $\underline{V}^{d'}$ be a non-trivial subspace of $\bar{D}$ which is spanned by the orthonormal basis $\vec{b}_1, \ldots, \vec{b}_{d'}$, while the space orthogonal to $\underline{V}^{d'}$ is spanned by $\vec{c}_{d'+1}, \ldots, \vec{c}_d$. If we represent the matrices $\tilde{D}_i$ in this basis, we find the matrix element

$$\vec{c}_l^{\,\dagger} \cdot \underbrace{\tilde{D}_i \cdot \vec{b}_{l'}}_{\equiv \vec{b} \in \underline{V}^{d'}} = \vec{c}_l^{\,\dagger} \cdot \vec{b} = 0 \quad (\forall l, l') \ .$$

In the last step we have used that $\vec{c}_l^{\,\dagger} \cdot \vec{b}$ is the inner product in a complex vector space and $\vec{c}_l$ is orthogonal to all $\vec{b}_{l'}$ and therefore also to $\vec{b}$. To determine the opposite matrix elements $\vec{b}_l^{\,\dagger} \cdot \tilde{D}_i \cdot \vec{c}_{l'}$ we first transpose it (recall that the transpose of a number is invariant),

$$\vec{b}_l^{\,\dagger} \cdot \tilde{D}_i \cdot \vec{c}_{l'} = \vec{c}_{l'}^{\,\mathrm{T}} \cdot \tilde{D}_i^{\mathrm{T}} \cdot \left(\vec{b}_l^{\,\dagger}\right)^{\mathrm{T}} = (\vec{c}_{l'}^{\,\dagger} \cdot \tilde{D}_i^{\dagger} \cdot \vec{b}_l)^* \ . \tag{4.8}$$

Now we use the unitarity of $\tilde{D}_i$,

$$\vec{c}_{l'}^{\,\dagger} \cdot \tilde{D}_i^{\dagger} \cdot \vec{b}_l = \vec{c}_{l'}^{\,\dagger} \cdot \underbrace{\tilde{D}_i^{-1} \cdot \vec{b}_l}_{\equiv \vec{b} \in \underline{V}^{d'}} = \vec{c}_l^{\,\dagger} \cdot \vec{b} = 0 \quad (\forall l, l') \ ,$$

which proves that (4.8) vanishes. With this result, we have shown that after a basis transformation into the basis $\vec{b}_1, \ldots, \vec{b}_{d'}, \vec{c}_{d'+1}, \ldots, \vec{c}_d$, every matrix is block diagonal (i.e. $\bar{D}$ is reducible) in contradiction to the assumption. $\surd$

4.1.2.1 Schur's Lemma, Part One

Suppose we have two irreducible matrix groups, $\bar{D}$ and $\bar{D}'$, with the same order g but, in general, different dimensions d and d'. If there exists a $(d \times d')$-dimensional matrix $\tilde{S}$ such that

$$\tilde{S} \cdot \tilde{D}'_i = \tilde{D}_i \cdot \tilde{S} \quad \forall i \ , \tag{4.9}$$

then it is either

(i) $\tilde{S} = \tilde{0}$, or
(ii) $\tilde{S}$ is square and non-singular, i.e. $\bar{D}$ and $\bar{D}'$ are equivalent.

Proof

(i) Let $\vec{s}_k$ be the d' columns of $\tilde{S}$ and $\underline{V}^{\bar{d}}$ $(\bar{d} \leq d)$ the space spanned by all $\vec{s}_k$. As a first step we want to show that it is either $\bar{d} = d$ or $\bar{d} = 0$. Equation (4.9), expressed by the vectors $\vec{s}_k$, has the following form

$$\sum_{k'} (\tilde{D}'_i)_{k',k} \vec{s}_{k'} = \tilde{D}_i \cdot \vec{s}_k \qquad (\forall k = 1, \ldots, d') \ . \tag{4.10}$$

The left-hand side of (4.10) is evidently an element of $\underline{V}^{\bar{d}}$. Consequently, for all i, $\tilde{D}_i \cdot \vec{s}_k$ must also be in $\underline{V}^{\bar{d}}$. Thus, either $\bar{d} = d$ or $d = 0$, as otherwise there would exist a non-trivial subspace that is invariant under all $\tilde{D}_i$, which contradicts the irreducibility of $\tilde{D}_i$. We shall examine both possibilities:

(a) When $\bar{d} = d$, it follows that $d' \geq d$ since d' vectors $\vec{s}_k$ cannot span a d-dimensional vector space $\underline{V}^{d}$.
(b) If $\bar{d} = 0$ it must be $\tilde{S} = \tilde{0}$.

(ii) If we take the adjoint of (4.9) and follow the same arguments as in case (i), we obtain either $\bar{d} = d'$, which implies $d \geq d'$, or $\tilde{S} = \tilde{0}$. Here we have used the fact that, if $\bar{D}$ is an irreducible matrix group, then its adjoint group $\bar{D}^{\dagger} \equiv \tilde{D}_1^{\dagger}, \ldots, \tilde{D}_g^{\dagger}$ is also irreducible.

The results from i) and ii) combined mean that it is either $d = d' = \bar{d}$ (and $\tilde{S}$ is then non-singular) or $\tilde{S} = \tilde{0}$. $\surd$

4.1.2.2 Schur's Lemma, Part Two

Let $\bar{D}$ be an irreducible matrix group. If there is a square matrix $\tilde{S} \neq \tilde{0}$ which commutes with all $\tilde{D}_i \in \bar{D}$,

$$\tilde{D}_i \cdot \tilde{S} = \tilde{S} \cdot \tilde{D}_i \quad \forall i \ ,$$

then $\tilde{S}$ is a multiple of the identity matrix,

$$\tilde{S} = \lambda \cdot \tilde{1} \ . \tag{4.11}$$

Proof Let $\lambda \in \mathbb{C}$ be an eigenvalue of $\tilde{S}$. Then $\tilde{S}' \equiv \tilde{S} - \lambda \cdot \tilde{1}$ also commutes with all $\tilde{D}_i$. However, $\tilde{S}'$ is singular, and therefore it is $\tilde{S}' = \tilde{0}$ because of the first part of Schur's lemma, which proves (4.11). $\surd$

4.2 Representations

Representations of groups play a crucial role in establishing the relationship between group theory and its applications in physics. Let G be a group and $\bar{\Gamma}$ a matrix group. If there exists a homomorphic map $f : G \to \bar{\Gamma}$, then f is said to be a representation of G. By definition, a homomorphic map satisfies the following condition:

$$\tilde{\Gamma}(a \cdot b) = \tilde{\Gamma}(a) \cdot \tilde{\Gamma}(b) \quad \forall\, a, b \in G \ . \tag{4.12}$$

For those new to this field, it can be confusing that the same term 'representation' is used for both the map f itself and the image of the map, which is the matrix group $\bar{\Gamma}$.

To get a first impression of the concept of representations of groups, we introduce some additional definitions and remarks:

(i) A representation is not necessarily bijective, i.e. two elements $a \neq b \in G$ can be assigned the same matrix. For example,

$$\tilde{\Gamma}(a) = \tilde{1} \quad \forall\, a \in G\ ,$$

is always a representation (with matrices $\tilde{1}$ of arbitrary dimension). The special case that $\tilde{1} = 1$ is a number is also referred to as a *one-representation*. We will encounter this representation a few times in later chapters.

(ii) If the map f is bijective, the representation $\bar{\Gamma}$ is isomorphic to G and is then called *faithful*. This means that in the case of point groups, the three-dimensional matrices that define such a group can also be interpreted as representations of themselves. This will indeed become relevant, e.g. in Chap. 9.

(iii) The following obviously applies to all representations

$$\tilde{\Gamma}(E) = \tilde{1} \quad , \quad \tilde{\Gamma}(a^{-1}) = (\tilde{\Gamma}(a))^{-1}\ .$$

(iv) The terminology of 'equivalence', 'reducibility' and other related concepts are carried over from matrix groups to representations without any modification.

(v) One-dimensional representations are always unitary, i.e. they have the form

$$\Gamma(a) = e^{\mathrm{i}\varphi(a)} \quad , \quad \varphi(a) \in \mathbb{R}\ ,$$

because for every $a \in G$ there is an n with $a^n = E$. Then (4.12) leads to $\Gamma(a)^n = 1$ which proves the statement.

(vi) Two one-dimensional representations $\bar{\Gamma}$ and $\bar{\Gamma}'$ with $\Gamma(a) \in \mathbb{C}$ are equivalent if and only if they are equal. This is because, in the case of equivalence, the matrix $\tilde{S}$ becomes a number $s \in \mathbb{C}$, which implies that $\bar{\Gamma}$ and $\bar{\Gamma}'$ are equal, for

$$\Gamma(a) = s^{-1} \cdot \Gamma'(a) \cdot s = \Gamma'(a) \qquad \forall a \in G\ .$$

(vii) A cyclic group of order g with the generating element a obviously has the g irreducible representations ($p = 1, \ldots, g$)

$$\Gamma_p(a) = \exp\left(\frac{2\pi\mathrm{i}}{g} \cdot p\right) \quad , \quad \Gamma_p(a^m) = \exp\left(\frac{2\pi\mathrm{i}}{g} \cdot p \cdot m\right)\ . \tag{4.13}$$

We will later show that every Abelian group of order g has exactly g inequivalent irreducible representations, as is the case here.

(viii) As we will show in Exercise 5.2.3 of Chap. 5, non-Abelian groups have at least one irreducible representation that is not one-dimensional.

Example

As an example, we consider the group D_3 (see Sects. 2.2.3 and 3.1),

$$D_3 = \underbrace{\{E\}}_{\equiv \mathcal{C}_1} \cup \underbrace{\{\delta_3, \delta_3^2\}}_{\equiv \mathcal{C}_2} \cup \underbrace{\{\delta_{21}, \delta_{22}, \delta_{23}, \}}_{\equiv \mathcal{C}_3} \ .$$

It has the following three inequivalent, irreducible representations[2]

(i) dimension $d = 1$, representation $\bar{\Gamma}^A$: $\Gamma(a) = 1, \forall a \in D_3$,
(ii) dimension $d = 1$, representation $\bar{\Gamma}^B$: $\Gamma(\mathcal{C}_1) = 1, \Gamma(\mathcal{C}_2) = 1, \Gamma(\mathcal{C}_3) = -1$,
(ii) dimension $d = 2$, representation $\bar{\Gamma}^E$:

$$\begin{aligned} &\mathcal{C}_1 : \tilde{\Gamma}(E) = \tilde{1} \ , \\ &\mathcal{C}_2 : \tilde{\Gamma}(\delta_3) = \tilde{D}_2 \ , \ \tilde{\Gamma}(\delta_3^2) = \tilde{D}_3 \ , \\ &\mathcal{C}_3 : \tilde{\Gamma}(\delta_{21}) = \tilde{D}_4 \ , \ \tilde{\Gamma}(\delta_{22}) = \tilde{D}_5 \ , \ \tilde{\Gamma}(\delta_{23}) = \tilde{D}_6 \ , \end{aligned} \tag{4.14}$$

with the matrices $\tilde{D}_i$ introduced in (2.16). The representation $\bar{\Gamma}^E$ is therefore faithful as shown in Exercise 5 of Chap. 2.

In the following, we will present three theorems that are best proved together. Their proof will be provided in Chap. 5 in connection with the proof of essential orthogonality theorems.

Theorem 1 *The number of inequivalent representations of a group is equal to the number of its classes.*[3]

The *character* $\chi(a)$ of a group element a in a (not necessarily irreducible) representation $\bar{\Gamma}$ is defined as

$$\chi(a) \equiv \mathrm{Tr}(\tilde{\Gamma}(a)) \ . \tag{4.15}$$

The set of all characters is called the *character of the representation*. Equivalent representations obviously have the same character. All elements $a \in G$ that belong to the same class have the same character in a representation.

Proof (of the latter statement) Let a, a' be in the same class, i.e. there is b with $b^{-1} \cdot a \cdot b = a'$. Then it is

$$\tilde{\Gamma}(a') = \tilde{\Gamma}(b)^{-1} \cdot \tilde{\Gamma}(a) \cdot \tilde{\Gamma}(b) \quad \Rightarrow \quad \mathrm{Tr}(\tilde{\Gamma}(a')) = \mathrm{Tr}(\tilde{\Gamma}(b)^{-1} \cdot \tilde{\Gamma}(a) \cdot \tilde{\Gamma}(b)) \ .$$

[2] As we shall see in Chap. 6, the inequivalent irreducible representations of a symmetry group are of crucial importance in physical applications and will therefore be the subject of much of this book. For this reason, in the following, we will normally mean the inequivalent irreducible representations when we use the term 'representations of a group'. Conversely, we will point out when a representation is not irreducible.

[3] See Fotnote 2.

Table 4.1 Character table of the group D_3

D_3	C_1	C_2	C_3
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

The invariance of the trace under cyclic permutations then proves the statement. $\surd$

Each group is associated with a unique square character table based on the previous statement and Theorem 1. For instance, the character table for D_3 with $\omega + \omega^2 = -1$ can be obtained using the representation matrices (4.14) and is shown in Table 4.1. Usually, the first column displays the characters of the class $C_1 = \{E\}$, indicating the dimension of the representation. In Chap. 7, we will discuss the character tables of the 32 point groups in solids in greater detail.

The *reduction of a reducible representation* $\bar{\Gamma}$ means finding a matrix $\tilde{S}$ such that

$$\tilde{S}^{-1} \cdot \bar{\Gamma} \cdot \tilde{S} = \underbrace{\bar{\Gamma}^1 \oplus \ldots \bar{\Gamma}^1}_{n_1 \text{ times}} \oplus \underbrace{\bar{\Gamma}^2 \oplus \ldots \bar{\Gamma}^2}_{n_2 \text{ times}} \ldots \oplus \underbrace{\bar{\Gamma}^r \oplus \ldots \bar{\Gamma}^r}_{n_r \text{ times}} , \tag{4.16}$$

where the $\bar{\Gamma}_p$ are the irreducible representations of a group and occur n_p times. We will use

$$\bar{\Gamma} = \sum_{p=1}^{r} n_p \bar{\Gamma}_p ,$$

as an abbreviation for (4.16) throughout this book, in accordance with large parts of the literature.

Theorem 2 *The reduction of a reducible representation is unambiguous except for the sequence and equivalence transformations of the representations* $\bar{\Gamma}^p$.

Let $G = \{a_1, \ldots, a_g\}$ be a group. Then, for every $a_i \in G$ is

$$a_i \cdot a_j = \sum_l \Gamma^{(\mathrm{r})}_{l,j}(a_i) \cdot a_l , \tag{4.17}$$

where the matrix elements $\Gamma^{(\mathrm{r})}_{l,j}(a_i)$ for a fixed j, i are non-zero (and equal to 1) for exactly one value of l and the sum sign, as has often been the case, has the meaning of a union of sets. The matrices $\tilde{\Gamma}(a_i)$ form the (faithful) so-called *regular representation* $\bar{\Gamma}^{(\mathrm{r})}$ of G. For example, the regular representation matrices of D_2 are (compare the multiplication Table 2.3) $\tilde{\Gamma}^{(\mathrm{r})}(E) = \tilde{1}$ and

$$\tilde{\Gamma}^{(\mathrm{r})}(\delta_{2x}) = \begin{pmatrix} 0&1&0&0\\ 1&0&0&0\\ 0&0&0&1\\ 0&0&1&0 \end{pmatrix} \quad , \quad \tilde{\Gamma}^{(\mathrm{r})}(\delta_{2y}) = \begin{pmatrix} 0&0&1&0\\ 0&0&0&1\\ 1&0&0&0\\ 0&1&0&0 \end{pmatrix} \quad , \quad \tilde{\Gamma}^{(\mathrm{r})}(\delta_{2z}) = \begin{pmatrix} 0&0&0&1\\ 0&0&1&0\\ 0&1&0&0\\ 1&0&0&0 \end{pmatrix} \quad .$$

Proof (of the previous statement) We prove successively the representation property and the isomorphism

(i) To show that $\bar{\Gamma}^{(\mathrm{r})}$ is a representation, we multiply (4.17) from the left with another element a_k,

$$\begin{aligned} a_k \cdot (a_i \cdot a_j) &\overset{(4.7)}{=} \sum_l \Gamma^{(\mathrm{r})}_{l,j}(a_i) \cdot a_k \cdot a_l \overset{(4.6)}{=} \sum_l \Gamma^{(\mathrm{r})}_{l,j}(a_i) \cdot \sum_m \Gamma^{(\mathrm{r})}_{m,l}(a_k) \cdot a_m \\ &= \sum_m \Big[\sum_l \Gamma^{(\mathrm{r})}_{l,j}(a_i) \cdot \Gamma^{(\mathrm{r})}_{l,j}(a_i) \Big] \cdot a_m \ . \end{aligned} \tag{4.18}$$

The brackets on the left side of this equation are, of course, meaningless because of the associative law and it is equal to

$$(a_k \cdot a_i) \cdot a_j \overset{(4.17)}{=} \sum_m \Big[\Gamma^{(\mathrm{r})}_{m,j}(a_k \cdot a_i) \Big] \cdot a_m \ . \tag{4.19}$$

A comparison of (4.18) and (4.19) then proves that

$$\tilde{\Gamma}^{(\mathrm{r})}(a_k \cdot a_i) = \tilde{\Gamma}^{(\mathrm{r})}(a_k) \cdot \tilde{\Gamma}^{(\mathrm{r})}(a_i) \ .$$

(ii) If G and $\bar{\Gamma}^{(\mathrm{r})}$ were not isomorphic there would be at least two elements $a_i \neq a_i'$ with $\tilde{\Gamma}^{(\mathrm{r})}(a_i) = \tilde{\Gamma}^{(\mathrm{r})}(a_j)$. But then, because of (4.17),

$$a_i \cdot a_j = a_i' \cdot a_j \quad \Rightarrow \quad a_i = a_i' \ ,$$

which leads to a contradiction.

Similar to Schur's lemma, we will need the regular representation only in the proofs in Chap. 5, but it will not play a role in the rest of the book.

Theorem 3 *The reduced form of the regular representation $\bar{\Gamma}^{(\mathrm{r})}$ of a group G contains each of the irreducible representations $\bar{\Gamma}^{p}$ of G exactly d_p times, where d_p is the dimension of the irreducible representation $\bar{\Gamma}^{p}$.*

Since the reduced representations have the same dimensions as the original representation (see (4.16)), the following equation results from Theorems 1 and 3

$$g = \sum_{p=1}^{r} d_p^2 \ , \tag{4.20}$$

Table 4.2 Solutions of (4.20) for all relevant values of g and class numbers r = 1,…, 10. For $g = 48$ we only show the solutions with the class number $r = 10$ of the group O_h

Order	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	Groups
1	1										C_1
2	1	1									C_2, C_i, C_s
3	1	1	1								C_3
4	1	1	1	1							$C_4, S_4, D_2, C_{2h}, C_{2v}$
6	1	1	2								D_3, C_{3v}
6	1	1	1	1	1	1					C_6, S_6, C_{3h}
8	1	1	1	1	2						D_4, C_{4v}, D_{2d}
8	1	1	1	1	1	1	1	1			C_{4h}, D_{2h}
12	1	1	1	3							T
12	1	1	1	1	2	2					$D_6, D_{3d}, C_{6v}, D_{3h}$
12	1	1	1	1	1	1	1	1	2		C_{6h}
12	1	1	1	1	1	1	1	1	1	1	
16	1	1	1	2	3						
16	1	1	1	1	2	2	2				
16	1	1	1	1	1	1	1	3			
16	1	1	1	1	1	1	1	1	2	2	D_{4h}
24	1	1	2	3	3						O, T_d
24	1	1	1	1	2	4					
24	1	1	1	2	2	2	3				
24	1	1	1	1	1	1	3	3			T_h
24	1	1	1	1	1	1	1	1	4		
24	1	1	1	1	2	2	2	2	2		D_{6h}
24	1	1	1	1	1	1	1	2	2	3	
48	1	1	1	1	1	1	1	3	4	4	
48	1	1	1	1	1	1	2	2	3	5	
48	1	1	1	1	2	2	3	3	3	3	O_h
48	1	1	1	2	2	2	2	2	3	4	

where r is the number of classes of G. This equation, along with the information about the class number, determines the dimensions of almost all representations uniquely for the 32 point groups in solids. Table 4.2 displays the solutions of (4.20) for all relevant values of g. Ambiguity only arises if there are two solutions for the same g and r, which is not the case for the class numbers found in the 32 point groups, except for the groups D_{6h} and O_h.

Equation (4.20) also has a consequence for the irreducible representations of Abelian groups since for these groups, $r = g$. Therefore, it follows that

$$d_p = 1 \quad \forall p = 1, \ldots, g \ ,$$

i.e. Abelian groups have only one-dimensional representations.

Chapter 5
Orthogonality Theorems

This chapter centers on the crucial orthogonality theorems for irreducible representation matrices and their characters. We begin by proving the orthogonality theorem for representation matrices in Sect. 5.1. Next, in Sect. 5.2, we set up the orthogonality theorems for the characters. The proof of these theorems follows, along with a revisit to the still-unproven theorems 1–3 from Chap. 4.

5.1 The Fundamental Theorem in the Theory of Representations

Let $\bar{\Gamma}^p$ and $\bar{\Gamma}^{p'}$ be inequivalent (if $p \neq p'$) and irreducible representations of a group G of order g. Then the *fundamental theorem in the theory of representations* states that

$$\sum_{a \in G} \Gamma^p_{i,j}(a) \cdot \Gamma^{p'}_{k,l}(a^{-1}) = \frac{g}{d} \delta_{i,l} \delta_{j,k} \delta_{p,p'} \ . \tag{5.1}$$

Here d, d' are the dimensions of $\bar{\Gamma}^p$, $\bar{\Gamma}^{p'}$. The perceived lack of symmetry on the right-hand side of the equation with respect to d and d' is resolved by the fact that the right-hand side is only non-zero when $p = p'$ and, consequently, $d = d'$. Therefore, it is possible to substitute d^{-1} with $\sqrt{d \cdot d'}^{-1}$ to obtain symmetry in d and d' for the theorem. Despite this possibility, however, the formulation given in (5.1) remains prevalent in the literature.

It is worth noting that the theorem does not offer any statements if $\bar{\Gamma}^p$ and $\bar{\Gamma}^{p'}$ are equivalent or if one (or both) of the representations is (are) reducible. If one chooses $\bar{\Gamma}^p$ and $\bar{\Gamma}^{p'}$ as unitary, as it is always possible, then

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$$\Gamma_{k,l}(a^{-1}) = \left[\tilde{\Gamma}(a)^{-1}\right]_{k,l} = \left[\tilde{\Gamma}(a)^{\dagger}\right]_{k,l} = \Gamma_{l,k}(a)^* \ ,$$

and one obtains the alternative form

$$\sum_{a\in G} \Gamma^{p}_{i,j}(a) \cdot \left(\Gamma^{p'}_{l,k}(a)\right)^* = \frac{g}{d}\delta_{i,l}\delta_{j,k}\delta_{p,p'} \ , \tag{5.2}$$

for the theorem.

Proof Let $\tilde{Z}$ be an arbitrary $d \times d'$-matrix with which we define the matrix

$$\tilde{P} \equiv \sum_{a\in G} \tilde{\Gamma}^{p}(a) \cdot \tilde{Z} \cdot \tilde{\Gamma}^{p'}(a)^{-1} = \sum_{a\in G} \tilde{\Gamma}^{p}(a) \cdot \tilde{Z} \cdot \tilde{\Gamma}^{p'}\left(a^{-1}\right) \ . \tag{5.3}$$

This matrix has the following property,

$$\tilde{P} \cdot \tilde{\Gamma}^{p'}(b) = \tilde{\Gamma}^{p}(b) \cdot \tilde{P} \qquad (\forall b \in G) \ , \tag{5.4}$$

because

$$\begin{aligned}
\tilde{P} \cdot \tilde{\Gamma}^{p'}(b) &\overset{(5.3)}{=} \sum_{a\in G} \tilde{\Gamma}^{p}(a) \cdot \tilde{Z} \cdot \tilde{\Gamma}^{p'}(a)^{-1} \cdot \tilde{\Gamma}^{p'}(b) \\
&= \tilde{\Gamma}^{p}(b) \cdot \sum_{a\in G} \left[\tilde{\Gamma}^{p}(b)^{-1} \cdot \tilde{\Gamma}^{p}(a)\right] \cdot \tilde{Z} \cdot \left[\tilde{\Gamma}^{p'}(b)^{-1} \cdot \tilde{\Gamma}^{p'}(a)\right]^{-1} \\
&= \tilde{\Gamma}^{p}(b) \cdot \sum_{a\in G} \tilde{\Gamma}^{p}(b^{-1} \cdot a) \cdot \tilde{Z} \cdot \tilde{\Gamma}^{p'}(b^{-1} \cdot a)^{-1} \\
&\overset{(2.4)}{=} \tilde{\Gamma}^{p}(b) \cdot \tilde{P} \ ,
\end{aligned}$$

where in the last line we use the rearrangement theorem (2.4). Equation (5.4) holds for any $\tilde{Z}$. We choose the matrix elements as

$$Z_{m,n} \equiv \delta_{m,j}\delta_{n,k} \ , \tag{5.5}$$

with fixed values of j, k, i.e. the matrix $\tilde{Z}$ has only one non-vanishing matrix element $Z_{j,k} = 1$. With (5.4) and Schur's lemma, we can then conclude

(i) if $\bar{\Gamma}^{p}$ and $\bar{\Gamma}^{p'}$ are irreducible and inequivalent it must be $\tilde{P} = \tilde{0}$ due to the first part of Schur's lemma. This leads to

$$0 = P_{i,l} \overset{(5.3)}{=} \sum_{a\in G}\sum_{m,n} \Gamma^{p}_{i,m}(a) Z_{m,n} \Gamma^{p'}_{n,l}\left(a^{-1}\right) \overset{(5.5)}{=} \sum_{a\in G} \Gamma^{p}_{i,j}(a) \Gamma^{p'}_{k,l}\left(a^{-1}\right) \ . \tag{5.6}$$

(ii) if $p = p'$ and $\bar{\Gamma}^p$ is irreducible, (5.4) and the second part of Schur's lemma demand that

$$\tilde{P} = \lambda \cdot \tilde{1} \ . \tag{5.7}$$

With the trace of both sides of this equation we find

$$\underbrace{\underbrace{\mathrm{Tr}(\tilde{P})}_{=g\,\mathrm{Tr}(\tilde{Z})}}_{=\delta_{j,k}} = \lambda \underbrace{\mathrm{Tr}(\tilde{1})}_{=d} \quad \Rightarrow \quad \lambda = \frac{g}{d}\delta_{j,k} \ .$$

The result for λ, inserted in (5.7) gives

$$P_{i,l} = \frac{g}{d}\delta_{j,k}\delta_{i,l} \overset{(5.3)/(5.5)}{=} \sum_{a\in G}\sum_{a\in G} \Gamma^p_{i,j}(a)\Gamma^p_{k,l}\left(a^{-1}\right) \ . \tag{5.8}$$

Equations (5.6) and (5.8) combined prove the fundamental theorem (5.1) in the theory of representations. In Exercise 5 we prove that the converse is also true, i.e. that a representation that satisfies (5.1) (with $p = p'$) must be irreducible. $\surd$

5.2 Consequences

5.2.1 *Theorem 4: Orthogonality of the Characters*

Let $\bar{\Gamma}^p$ be the representations of a group G of order g and χ^p_i its characters. Due to Theorem 1, which we will prove in the following Sect. 5.2.2, we have $i,\ p = 1, \ldots, r$, where r is the number of classes of G, as always. Under these conditions, the following two orthogonality theorems hold,

$$g \cdot \delta_{p,q} = \sum_{i=1}^{r} r_i \cdot \left(\chi^p_i\right)^* \cdot \chi^q_i \ , \tag{5.9}$$

$$\frac{g}{r_i} \cdot \delta_{i,j} = \sum_{p=1}^{r} \left(\chi^p_i\right)^* \cdot \chi^p_j \ , \tag{5.10}$$

where r_i is the number of elements in the i-th class.

5.2.2 *Proof of Theorems 1–4*

We prove the Theorems 1–4 in 4 steps.

(i) We consider only unitary representations $\bar{\Gamma}^p$, which is possible because every representation is equivalent to a unitary one (see Sect. 4.1.1) and the corresponding character χ^p is invariant under similarity transformations. For each (not necessarily irreducible) representation $\bar{\Gamma}$, we define the r-dimensional character vector

$$\vec{v}^{\Gamma} \equiv \left(\sqrt{\frac{r_1}{g}} \chi_1^{\Gamma}, \ldots, \sqrt{\frac{r_r}{g}} \chi_r^{\Gamma} \right)^T . \tag{5.11}$$

If $\bar{\Gamma} = \bar{\Gamma}^p$ is irreducible, it holds for the associated character vector $\vec{v}^p$ that

$$\left(\vec{v}^p\right)^{\dagger} \cdot \vec{v}^q = \delta_{p,q} .$$

To prove this equation, we evaluate the left hand side,

$$\left(\vec{v}^p\right)^{\dagger} \cdot \vec{v}^q \overset{(5.11)}{=} \sum_i^r \frac{r_i}{g} \cdot \left(\chi_i^p\right)^* \cdot \chi_i^q = \frac{1}{g} \sum_a \left(\chi_i(a)\right)^* \cdot \chi_i(a) ,$$

where a are the elements of the group. With the definition (4.15) of the character we then find

$$\left(\vec{v}^p\right)^{\dagger} \cdot \vec{v}^q = \frac{1}{g} \sum_{i=1}^{d_p} \sum_{j=1}^{d_q} \Gamma_{i,i}^p(a^{-1}) \cdot \Gamma_{j,j}^p(a) \overset{(5.1)}{=} \delta_{p,q} \frac{1}{d} \sum_{i=1}^{d_p} = \delta_{p,q} \cdot \surd \tag{5.12}$$

Equation (5.12) establishes the validity of (5.9). Conversely, it can be deduced that the maximum number of irreducible representations is r, based on the fact that an r-dimensional space can contain no more than r orthogonal vectors $\vec{v}^p$. In order to prove Theorem 1, it is necessary to demonstrate that there are also at least r irreducible representations, which will bring the total number to exactly r. This will be done in connection with point (iii). However, before that, we address Theorem 3.

(ii) Let

$$\bar{\Gamma}^{(\mathrm{r})} = \sum_p n_p^{(\mathrm{r})} \cdot \bar{\Gamma}^p ,$$

be the reduction of the regular representation. The same relation then applies to the corresponding character vectors

$$\vec{v}^{(\mathrm{r})} = \sum_p n_p^{(\mathrm{r})} \cdot \vec{v}^p , \tag{5.13}$$

where $\sum_p$ now represents a real sum over the irreducible representations. In (5.13) we have used (4.16) and the fact that

$$\mathrm{Tr}(\tilde{S}^{-1} \cdot \tilde{\Gamma}^{(\mathrm{r})}(a) \cdot \tilde{S}) = \mathrm{Tr}(\tilde{\Gamma}^{(\mathrm{r})}(a)) = \sum_p n_p^{(\mathrm{r})} \cdot \mathrm{Tr}(\tilde{\Gamma}^p(a)) = \sum_p n_p^{(\mathrm{r})} \cdot \chi^p(a) \ .$$

Multiplying (5.13) with $(\vec{v}^q)^\dagger$ from the left then gives

$$\left(\vec{v}^q\right)^\dagger \cdot \vec{v}^{(\mathrm{r})} = \sum_p n_p^{(\mathrm{r})} \cdot \left(\vec{v}^q\right)^\dagger \cdot \vec{v}^p \overset{(5.13)}{\Rightarrow} n_p^{(\mathrm{r})} = \left(\vec{v}^p\right)^\dagger \cdot \vec{v}^{(\mathrm{r})} \ . \tag{5.14}$$

The regular representation is defined such that

$$\vec{v}^{(\mathrm{r})} = (\sqrt{g}, 0, \ldots, 0)^T \ , \tag{5.15}$$

where the class of the identity element is chosen as the first component. It is worth noting that the character of E always corresponds to the dimension of the representation, which implies that $\chi^{(\mathrm{r})}(E) = g$ and $r_1 = r_E = 1$. In addition, we have $\chi_1^p = \chi^p(E) = d_p$, which, when combined with (5.14), leads to:

$$n_p^{(\mathrm{r})} = d_p \ . \tag{5.16}$$

This proves Theorem 3. The components of the vector (5.13) are then given as

$$\sqrt{g} \cdot \delta_{i,1} = \frac{\sqrt{r_i}}{\sqrt{g}} \sum_p d_p \cdot \chi_i^p \ ,$$

where we have used (5.15) and (5.16). Since the left side of this equation is zero for $i \neq 1$ and $r_1 = 1$, we can cancel $\sqrt{r_i}$ on the right side. With that, we find

$$\sum_p d_p \cdot \chi_i^p = g \cdot \delta_{i,1} \ , \tag{5.17}$$

which is an auxiliary equation that we need in the next part of the proof.

(iii) For each class $\mathcal{C}_j$ we define, with respect to a representation $\bar{\Gamma}$ of dimension d, the matrix

$$\tilde{S}_j \equiv \sum_{a \in \mathcal{C}_j} \tilde{\Gamma}(a) \ . \tag{5.18}$$

This matrix commutes with every matrix $\tilde{\Gamma}(b)$, because it is

$$\tilde{\Gamma}(b)^{-1} \cdot \tilde{S}_j \cdot \tilde{\Gamma}(b) \overset{(5.18)}{=} \sum_{a \in \mathcal{C}_j} \tilde{\Gamma}(b^{-1} \cdot a \cdot b) \overset{(2.6)}{=} \tilde{S}_j \ .$$

Then we can deduce from Schur's lemma (part two)

$$\tilde{S}_j = \mu_j \cdot \tilde{1} \ .$$

Especially for the irreducible representations $\bar{\Gamma}^p$ with dimension d_p we find the matrices

$$\tilde{S}_j^p = \mu_j^p \cdot \tilde{1} \ . \tag{5.19}$$

The trace of the two sides of this equation and

$$\sum_{a \in \mathcal{C}_j} 1 = r_j \ ,$$

yields

$$\mu_j^p = \frac{r_i \chi_i^p}{d_p} \ . \tag{5.20}$$

On the other hand, because of the definition of (5.18), it is

$$\tilde{S}_i^p \cdot \tilde{S}_j^p = \sum_{\substack{a \in \mathcal{C}_i \\ b \in \mathcal{C}_j}} \tilde{S}^p(a \cdot b) \overset{(2.8)}{=} \sum_{k=1}^{r} f_{ijk} \cdot \tilde{S}_k \ ,$$

where f_{ijk} are the multiplication coefficients introduced in Sect. 2.3.3. With (5.19) and (5.20) we find

$$r_i \cdot r_j \cdot \chi_i^p \cdot \chi_j^p = d_p \sum_{k=1}^{r} c_{ijk} \cdot r_k \cdot \chi_k^p \ .$$

Next we carry out the sum over p on both sides and use (5.17),

$$r_i \cdot r_j \sum_p \chi_i^p \cdot \chi_j^p = c_{ij1} \cdot r_1 \cdot g \ .$$

Recall that $r_1 = 1$ and with (2.8) we obtain

$$\sum_p \chi_i^p \cdot \chi_j^p = \frac{g}{r_j} \delta_{i,\bar{j}} \overset{j \to \bar{j}}{\Longrightarrow} \sum_p \chi_i^p \cdot \chi_{\bar{j}}^p = \frac{g}{r_j} \delta_{i,j} \ , \tag{5.21}$$

where we have used that a class and its inverse have the same number of elements, $r_{\bar{j}} = r_j$. To finish this part of the proof, we have to evaluate $\chi_{\bar{i}}^p$ in (5.21). With $a \in \mathcal{C}_i$ and $a^{-1} \in \mathcal{C}_{\bar{j}}$ we show in Exercise 7 that

$$\chi_{\bar{j}}^{p} = \left(\chi_{j}^{p}\right)^{*} .$$

As a result of this, we can write

$$\sum_{p} \chi_{i}^{p} \cdot \left(\chi_{j}^{p}\right)^{*} = \frac{g}{r_j} \delta_{i,j} ,$$

which proves the orthogonality theorem (5.10). Using this equation, we have also demonstrated that in the matrix of character vectors $(\vec{v}^1, \ldots, \vec{v}^r)$, not only are all columns orthogonal, but so are all rows. This implies that the rows must have a minimum dimension of r, meaning there are at least r distinct character vectors. Since we have already established in (i) that there can be at most r distinct character vectors, we can now conclude that there are exactly r such vectors. This proves Theorem 1, which states that the number of classes corresponds to the number of irreducible representations.

(iv) Finally, we aim to prove Theorem 2, which concerns the uniqueness of the reduction of a representation. Let $\bar{\Gamma}$ be an arbitrary representation of a group G with order g and a reduced form

$$\bar{\Gamma} = \sum_{p=1}^{r} n_p \cdot \bar{\Gamma}^p .$$

Again, this equation translates into a corresponding equation for the characters

$$\chi_i = \sum_{p=1}^{r} n_p \cdot \chi_i^p , \tag{5.22}$$

where (as always) χ_i, χ_i^p are the characters of the class i. We multiply (5.22) with $r_i \left(\chi_i^p\right)^*$, sum over i, and use (5.9),

$$n_p = \frac{1}{g} \sum_{i=1}^{r} r_i \cdot \chi_i \cdot \left(\chi_i^p\right)^* . \tag{5.23}$$

The uniqueness of the right side of (5.23) implies that the left side, i.e. n_p, must also be uniquely defined, thereby proving Theorem 2.

Throughout this book, (5.23) will be highly useful as it allows us to determine how often an irreducible representation in the reduction of a reducible representation occurs. As a newcomer to the field, the reader may not yet see the utility in decomposing a representation into its irreducible components. However, the upcoming chapters will shed light on its significance in physics.

5.2.3 *Clear Criterion for the Irreducibility of a Representation*

Finishing this chapter, we aim to establish a useful criterion for easily determining whether a representation is reducible or irreducible. This criterion will be applied in several sections of this book. It states: The representation $\bar{\Gamma}$ of a group G is irreducible if and only if

$$\sum_{i=1} r_i \cdot |\chi_i|^2 = g \ , \tag{5.24}$$

holds for its characters, where g represents the order of the group. If the left side of (5.24) is greater than g, then the representation is reducible. Alternatively, (5.24) can be expressed as a sum over all group elements,

$$\sum_{a \in G} |\chi(a)|^2 = g \ . \tag{5.25}$$

Proof Let

$$\bar{\Gamma} = \sum_p n_p \cdot \bar{\Gamma}^p \ ,$$

again be the reduction of $\bar{\Gamma}$. Then it follows that

$$\sum_{i=1} r_i \cdot \chi_i^* \cdot \chi_i \overset{(5.22)}{=} \sum_{i=1} r_i \sum_{p,q} n_p \cdot n_q \cdot \left(\chi_i^p\right)^* \cdot \chi_i^q \overset{(5.9)}{=} g \sum_p n_p^2 \ . \tag{5.26}$$

If $\bar{\Gamma}$ is irreducible, only one n_p in (5.26) is non-zero and equal to 1. In all other cases, the sum over n_p^2 is greater then one. This proves the criterion. $\surd$

Example As an example, we can now verify that the representations of the group D_3 introduced in Sect. 4.2 are indeed irreducible. With Table 4.1 we find for the left side of (5.24)

$$\begin{aligned} A_1 &: 1 + 2 + 3 = 6 (= g) \ , \ \surd \\ A_2 &: 1 + 2 + 3 = 6 \ , \ \surd \\ E &: 1 \cdot 2^2 + 2 \cdot (-1)^2 = 6 \ . \ \surd \end{aligned}$$

Exercises

1. Let $G = G_1 \times G_2$ be a product group of two groups

$$G_1 = \{a_1 \ldots, a_{g_1}\},$$
$$G_2 = \{b_1 \ldots, b_{g_2}\},$$

and

$$\bar{\Gamma}^1 = \{\tilde{\Gamma}^1(a_1), \ldots, \tilde{\Gamma}^1(a_{g_1})\},$$
$$\bar{\Gamma}^2 = \{\tilde{\Gamma}^2(b_1), \ldots, \tilde{\Gamma}^2(b_{g_2})\},$$

(not necessarily irreducible) representations of G_1 and G_2.

(a) Show that two elements $(a_i; b_j)$ and $(a'_i; b'_j)$ of G are in a class (i.e. $(a_i; b_j) \sim (a'_i; b'_j)$) if, and only if $a_i \sim a'_i$ in G_1 and $b_j \sim b'_j$ in G_2. What classes are there in $G = G_1 \times G_2$ and how many elements does each class have?

(b) Show that the product matrices

$$\Gamma^{1\otimes 2}_{(ij),(kl)}(a_n b_m) \equiv \Gamma^1_{i,k}(a_n) \cdot \Gamma^2_{j,l}(b_m)$$

are a representation of the group G (*product representations*).

(c) Show that $\bar{\Gamma}^{1\otimes 2}$ is irreducible if $\bar{\Gamma}^1$ and $\bar{\Gamma}^2$ are irreducible (use the result from Sect. 5.2.3).

2. Using the result from Exercise 1, determine the irreducible representations of

$$D_{3d} = D_3 \times (E, I)\ .$$

Use the fact that (E, I) is isomorphic to C_2 (see Table 6.1) and the irreducible representations of D_3 (see the example in Sect. 4.2).

3. It is evident that a group comprising of orthogonal matrices,

$$G = \{\tilde{D}_1, \ldots, \tilde{D}_g\}\ ,$$

forms a (real, faithful) three-dimensional representation of the corresponding (abstract) point group (as explained in Sect. 3.5). This representation, however, is typically reducible. Determine the irreducible components of these representations for the groups D_2 and D_3.
Hint: A helpful approach is to employ (5.23) in combination with the character tables 5.1.

4. Let G' be a sub-group of a group G and $\bar{\Gamma}^p$ one of the irreducible representations of G. Then $\bar{\Gamma}^p$ is obviously also a (in general reducible) representation of G', the so-called 'subduced representation' $\bar{\Gamma}^{(s)}$. Determine for the group $G = D_3$ and its sub-groups

(a) $G' = \{E, \delta_3, \delta_3^2\}$,
(b) $G' = \{E, \delta_{2,x}\}$,

Table 5.1 Character tables of the groups D_2, D_3, C_3 ($\omega = e^{2\pi i/3}$)

D_2	E	$\delta_{2,x}$	$\delta_{2,y}$	$\delta_{2,z}$
A	1	1	1	1
B_1	1	-1	-1	1
B_2	1	-1	1	-1
B_3	1	1	-1	-1

D_3	E	$2\delta_3$	$3\delta_2$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

C_3	E	δ_3	δ_3^2
A	1	1	1
E_1	1	ω	ω^2
E_2	1	ω^2	ω

for all irreducible representations $\bar{\Gamma}^p$ of G, respectively, the irreducible components of the subduced representation $\bar{\Gamma}^{(s)} = \bar{\Gamma}^p$ with respect to G'.
Hint: Use (5.23) and the character tables of D_2, D_3, C_3, and C_2, see Tables 5.1 and 6.1.

5. A representation $\bar{\Gamma}$ satisfies relation (5.2), i.e.

$$\sum_{a\in G} \Gamma_{i,j}(a)\left(\Gamma_{l,k}(a)\right)^* = \frac{g}{d}\delta_{i,l}\delta_{j,k} \ .$$

Show that the representation is then irreducible.

6. Show that the representation of the group D_3,

$$\tilde{\Gamma}(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \ , \quad \tilde{\Gamma}(\delta_3) = \begin{pmatrix} 0 & 1 & 2 \\ \frac{3}{2} & 1 & 6 \\ \frac{1}{4} & -\frac{1}{2} & -1 \end{pmatrix} \ , \quad \tilde{\Gamma}(\delta_2^3) = \begin{pmatrix} 2 & 0 & 4 \\ 3 & -\frac{1}{2} & 3 \\ -1 & \frac{1}{4} & -\frac{3}{2} \end{pmatrix} \ ,$$

$$\tilde{\Gamma}(\delta_{21}) = \begin{pmatrix} 0 & 1 & 2 \\ 0 & 1 & 0 \\ \frac{1}{2} & -\frac{1}{2} & 0 \end{pmatrix} \ , \quad \tilde{\Gamma}(\delta_{22}) = \begin{pmatrix} 2 & 0 & 4 \\ \frac{3}{2} & 1 & 6 \\ -\frac{3}{4} & 0 & -2 \end{pmatrix} \ , \quad \tilde{\Gamma}(\delta_{23}) = \begin{pmatrix} 0 & 1 & 2 \\ 0 & 1 & 0 \\ \frac{1}{2} & -\frac{1}{2} & 0 \end{pmatrix} \ ,$$

is reducible. Which irreducible representations does it contain after a reduction?

7. Prove that inverse elements of a group have characters that are complex conjugate to each other in each representation.

8. Prove that the sum of the matrix elements of any irreducible representation over a group G is zero, i.e.

$$\sum_{a\in G} \Gamma^p_{i,j}(a) = 0 \ .$$

The only exception here is the trivial one-representation.

9. If a group G with g elements has g irreducible representations, is G then Abelian?

10. Explain why in every one-dimensional representation $\bar{\Gamma}$ the following is true for the inversion I and every mirror plane σ,

$$\Gamma(I) = \Gamma(\sigma) = \pm 1 \ .$$

11. Explain why a non-Abelian group cannot have exclusively one-dimensional irreducible representations.

Chapter 6
Quantum Mechanics and Group Theory

With the mathematical groundwork laid, we can now delve into the connection between group theory and quantum mechanics. Since we first have to go through the two more technical Sects. 6.1 and 6.2, we want to start by pointing out the main goal of this chapter: As we will see in Sect. 6.3, the eigenspaces of Hamiltonians are completely determined by group theory as far as their degeneracy and their symmetry properties are concerned. This will then be the basis of all other applications in later chapters.

In Sect. 6.1, we introduce the concept of representation spaces and explore their properties. To construct these spaces, we employ the projection operators introduced by Wigner [1] and examine their properties in Sect. 6.2. Finally, in Sect. 6.3, we analyze Hamiltonians with symmetries where we will find the strong connection with irreducible representations already mentioned above.

6.1 Representation Spaces

6.1.1 Definition of Representation Spaces

Let G be a group with elements $a \in G$, and $\hat{U}_a$ be a group of unitary operators on a Hilbert space $\underline{H}$ that is isomorphic to G, meaning that

$$\hat{U}_a \cdot \hat{U}_b = \hat{U}_{a \cdot b} \ ,$$

for all $a, b \in G$. In later applications, these operators will represent symmetry operators of a Hamiltonian. For our current considerations in Sect. 6.1, however, this is not yet relevant.

Assume that $\bar{\Gamma}$ is a d-dimensional representation of G. A set of elements $|\lambda\rangle$ from $\underline{H}$ is then called the *basic functions* of the representation $\bar{\Gamma}$ or *representation functions* if

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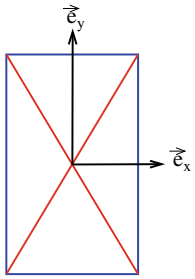

Fig. 6.1 A body which is left unchanged by the symmetry operations of the group C_2 and the coordinate system of the representation functions

Table 6.1 Character table of the group C_2

C_2	E	δ_2
A	1	1
B	1	-1

$$\hat{U}_a|\lambda\rangle = \sum_{\mu=1}^{d} \Gamma_{\mu,\lambda}(a)|\mu\rangle \qquad (\forall\lambda \text{ and } \forall a \in G) \; . \tag{6.1}$$

Obviously, if $\{|\lambda\rangle_1\}$ and $\{|\lambda\rangle_2\}$ are basis functions of the same representation $\bar{\Gamma}$, then

$$|\lambda\rangle = \alpha|\lambda\rangle_1 + \beta|\lambda\rangle_2 \; ,$$

are also such functions $\forall\alpha, \beta \in \mathbb{C}$. One usually says, $|\lambda\rangle$ *belongs to the* λ*-th row of the representation* $\bar{\Gamma}$.

Example As discussed in Sect. 1.2.1, a spatial rotation in space corresponds to a transformation $\Psi_1(\vec{r}) \to \Psi_2(\vec{r})$ in Hilbert space, defined by

$$\Psi_2(\vec{r}) \equiv \Psi_1(\tilde{D} \cdot \vec{r}) \; . \tag{6.2}$$

As a simple example, we consider the group C_2, the proper point symmetry group of a pyramid over a rectangle (see Fig. 6.1). It has two (one-dimensional) representations shown in Table 6.1. Due to the one-dimensionality of the representations, the characters here are identical to the representation matrices[1]

$$\Gamma^A : \Gamma^A_{1,1}(E) = 1 \; , \; \Gamma^A_{1,1}(\delta_2) = 1 \; ,$$
$$\Gamma^B : \Gamma^B_{1,1}(E) = 1 \; , \; \Gamma^B_{1,1}(\delta_2) = -1 \; ,$$

that describe the transformation behavior of representation functions. Examples for representation functions in the Hilbert space L^2 are

[1] We discuss the notation of the irreducible representations (i.e. here A and B) in Chap. 7.

$$\begin{aligned} \Gamma^A &: \Psi_A(\vec{r}) = f(|\vec{r}|) \quad \text{or} \quad \Psi_A(\vec{r}) = z \cdot f(|\vec{r}|) \ , \\ \Gamma^B &: \Psi_B(\vec{r}) = x \cdot f(|\vec{r}|) \quad \text{or} \quad \Psi_B(\vec{r}) = y \cdot f(|\vec{r}|) \ , \end{aligned} \tag{6.3}$$

where $f(|\vec{r}|)$ is any rotationally symmetric function in the Hilbert space L^2. To check whether Ψ_A and Ψ_B are representation functions, one must apply the symmetry operators $\hat{U}_a$ to them,

$$\begin{aligned} \hat{U}_E \Psi_A(\vec{r}) = \Psi_A(\vec{r}) \ , \quad \hat{U}_E \Psi_B(\vec{r}) = \Psi_B(\vec{r}) \ , \\ \hat{U}_{\delta_2} \Psi_A(\vec{r}) = \Psi_A(\vec{r}) \ , \quad \hat{U}_{\delta_2} \Psi_B(\vec{r}) = -\Psi_B(\vec{r}) \ . \surd \end{aligned}$$

6.1.2 *Representation Functions of Irreducible Representations*

The d basis functions of a d-dimensional irreducible representation $\bar{\Gamma}^p$ form an orthogonal function system.

Proof We consider the scalar product of two basis functions $|\lambda\rangle$, $|\mu\rangle$,

$$\langle \lambda | \mu \rangle = \frac{1}{g} \sum_{a \in G} \langle \lambda | \hat{U}_a^\dagger \cdot \hat{U}_a | \mu \rangle \ ,$$

where we have used that

$$1 = \hat{U}_a^\dagger \cdot \hat{U}_a = \frac{1}{g} \sum_{a \in G} \hat{U}_a^\dagger \cdot \hat{U}_a \ .$$

With (6.1) we then find

$$\langle \lambda | \mu \rangle = \frac{1}{g} \sum_{\lambda', \mu'} \sum_{a \in G} \left(\Gamma^p_{\lambda', \lambda}(a) \right)^* \cdot \Gamma^p_{\mu', \mu}(a) \cdot \langle \lambda' | \mu' \rangle \overset{(5.2)}{=} \frac{1}{d} \delta_{\lambda, \mu} \sum_{\lambda'} \langle \lambda' | \mu' \rangle \sim \delta_{\lambda, \mu} \ . \surd$$

In the following, we assume that the representation functions are normalized. The representation functions of a d-dimensional representation $\bar{\Gamma}$ form a basis for a d-dimensional subspace $\underline{V^d}$ of the Hilbert space $\underline{H}$. This subspace is referred to as the representation space of $\bar{\Gamma}$. It is possible for a representation to have multiple representation spaces, which may be infinite in number. For instance, there exists an infinite set of states of the form (6.3), since there are infinitely many functions $f(|\vec{r}|)$ that can be chosen to be orthogonal. On the other hand, a representation space uniquely determines the corresponding representation (up to equivalence).

Proof Let (6.1) be satisfied. Then we choose another basis $|\lambda\rangle_2$ of the representation space, thus

$$|\lambda\rangle_2 = \sum_{\lambda'} U_{\lambda',\lambda}|\lambda'\rangle \ .$$

Then,

$$\hat{U}_a|\lambda\rangle_2 = \sum_{\lambda'} U_{\lambda',\lambda} \cdot \hat{U}_a|\lambda'\rangle \overset{(6.1)}{=} \sum_{\lambda',\mu'} U_{\lambda',\lambda} \cdot \Gamma_{\mu',\lambda'}|\mu'\rangle \ .$$

We can now also express the state $|\mu'\rangle$ in reverse by $|\mu\rangle_2$,

$$|\mu'\rangle = \sum_{\mu} \left(\tilde{U}^{-1}\right)_{\mu,\mu'} |\mu\rangle_2 \ .$$

This leads to

$$\hat{U}_a|\lambda\rangle_2 = \sum_{\mu} \Gamma'_{\mu,\lambda}|\mu\rangle_2 \ ,$$

with

$$\bar{\Gamma}' = \tilde{U}^{-1} \cdot \bar{\Gamma} \cdot \tilde{U} \ ,$$

which proves the statement.

6.1.3 Representation Spaces and Invariant Sub-spaces

It is clear that every representation space is a subspace of $\underline{H}$ that is invariant (as defined in Sect. 4.1.2) under all operators $\hat{U}_a$. However, the converse is also true: every subspace $\underline{V}^d$ that is invariant under all $\hat{U}_a$ operators is a representation space.

Proof Let $|\lambda\rangle$ ($\lambda = 1, \ldots, d$) be a basis of $\underline{V}^d$. Then, the invariance means

$$\hat{U}_a|\lambda\rangle = \sum_{\lambda'} D_{\lambda',\lambda}(a)|\lambda'\rangle \ . \tag{6.4}$$

To prove the statement, we need to show the representation properties of the matrices $\tilde{D}(a)$:

$$\begin{aligned}\hat{U}_a \cdot \hat{U}_b|\lambda\rangle &= \sum_{\lambda''} D_{\lambda'',\lambda}(b) \cdot \hat{U}_a|\lambda''\rangle = \sum_{\lambda',\lambda''} D_{\lambda'',\lambda}(b) \cdot D_{\lambda',\lambda''}(a)|\lambda'\rangle \\ &= \hat{U}_{a\cdot b}|\lambda\rangle = \sum_{\lambda'} D_{\lambda',\lambda}(a \cdot b)|\lambda'\rangle \ .\end{aligned}$$

Therefore

$$D_{\lambda',\lambda}(a \cdot b) = \sum_{\lambda''} D_{\lambda',\lambda''}(a) \cdot D_{\lambda'',\lambda}(b) \ . \quad \surd$$

6.1.4 Irreducibility of Representation Spaces

If a representation space $\underline{V}^d$ of dimension d can be expressed as a direct sum of two representation spaces of smaller dimension, i.e.

$$\underline{V}^d = \underline{V}^{d_1} \oplus \underline{V}^{d_2} \quad (d_1 + d_2 = d) \ , \tag{6.5}$$

it is referred to as reducible.

Otherwise, it is called irreducible. The representation corresponding to $\underline{V}^d$ is reducible if and only if $\underline{V}^d$ itself is reducible.

Proof We have to give the proof in both directions:

(i) We assume that $\underline{V}^d$ is reducible and is spanned by the states $\{|\lambda\rangle\}$. Then we have to show that the representation $\bar{\Gamma}$ defined by the matrices $\tilde{\Gamma}(a)$ with the elements

$$\Gamma_{\lambda',\lambda}(a) \equiv \langle\lambda'|\hat{U}_a|\lambda\rangle \ ,$$

are reducible. Since $\underline{V}^d$ is reducible, there are bases $\{|\mu\rangle\}$ $(\mu = 1, \ldots, d_1)$ and $\{|\mu\rangle\}$ $(\mu = d_1 + 1, \ldots, d)$ that span representation spaces $\underline{V}^{d_1}$ and $\underline{V}^{d_2}$ with the property (6.5). The two bases are linked via some matrix $\tilde{S}$, i.e.

$$|\lambda\rangle = \sum_{\mu} S_{\mu,\lambda}|\mu\rangle \ . \tag{6.6}$$

The assumption that the bases are orthogonal does not limit the generality of the proof. Then, the matrix $\tilde{S}$ is unitary. With this and (6.4) we find $(\tilde{D} \to \tilde{\Gamma})$

$$\langle\lambda|\hat{U}_a|\lambda'\rangle = \Gamma_{\gamma,\gamma'}(a) \overset{(6.6)}{=} \sum_{\mu,\mu'} S^*_{\mu,\lambda} \cdot S_{\mu',\lambda'} \cdot \langle\mu|\hat{U}_a|\mu'\rangle \ .$$

In matrix form, this equation is given by $(\Gamma'_{\mu,\mu'}(a) \equiv \langle\mu|\hat{U}_a|\mu'\rangle)$

$$\tilde{S}^{-1} \cdot \tilde{\Gamma}'(a) \cdot \tilde{S} = \tilde{\Gamma}(a) \quad \Rightarrow \quad \tilde{\Gamma}'(a) = \tilde{S} \cdot \tilde{\Gamma}(a) \cdot \tilde{S}^{-1} \ .$$

Since $\bar{\Gamma}'$ is block diagonal, $\bar{\Gamma}$ is reducible. $\surd$

(ii) We assume that $\bar{\Gamma}$ is reducible and $\underline{V}$ is one of its representation spaces spanned by the vectors $\{|\lambda\rangle\}$. The proof that $\underline{V}$ is then reducible uses the same steps as under (i). Let $\tilde{S}$ be the (unitary) matrix that reduces $\bar{\Gamma}$. Then, one can easily show that in the base

$$|\mu\rangle = \sum_{\lambda} S_{\lambda,\mu}|\lambda\rangle \ ,$$

the matrix elements $\langle\mu|\hat{U}_a|\mu'\rangle$ are block diagonal for all a. $\surd$

Example As an example, let us look again at the group C_2. The two functions

$$\varphi_1(\vec{r}) \equiv (x+z)\,f(|\vec{r}|) \ ,$$
$$\varphi_2(\vec{r}) \equiv (x-z)\,f(|\vec{r}|) \ ,$$

form a two-dimensional representation space of this group. This space is obviously reducible, because it can also be spanned by the two irreducible (one-dimensional) representation spaces given by the states

$$\Psi_A(\vec{r}) = z \cdot f(|\vec{r}|) \quad \text{and} \quad \Psi_B(\vec{r}) = x \cdot f(|\vec{r}|) \ ,$$

which we have already introduced in Sect. 6.1.1.

6.1.5 The Expansion Theorem

If $\bar{\Gamma}^p$ $(p = 1, \ldots, r)$ are the representations (of dimension d_p) of a group G of operators $\hat{U}_a$, then every state $|\psi\rangle$ in the Hilbert space of these operators can be written as

$$|\psi\rangle = \sum_{p=1}^{r} \sum_{\lambda=1}^{d_p} |\lambda\rangle^p \ . \tag{6.7}$$

Here, the states $|\lambda\rangle^p$ belong to the λth line of the representation Γ^p. Before we prove the theorem, it is worth explaining a few things and looking at an example:

(i) We first have to clarify the meaning of the statement in the theorem that *the states $|\lambda\rangle^p$ belong to the λth line of the representation $\bar{\Gamma}$*. It means that $d_p - 1$ *partner functions* $|\lambda_i\rangle$ exist which together with $|\lambda\rangle^p$ form a representation space of $\bar{\Gamma}^p$ and in which $|\lambda\rangle^p$ belongs to the λth row, as defined in Sect. 6.1.1.

(ii) It is possible that not for each p and λ a state $|\lambda\rangle^p$ appears in the expansion (6.7). Formally, more precise would therefore be the formula

$$|\psi\rangle = \sum_{p=1}^{r} \sum_{\lambda=1}^{d_p} \alpha_\lambda^p |\lambda\rangle^p \ ,$$

with $\alpha_\lambda^p = 1$ or $\alpha_\lambda^p = 0$. In the literature, however, the shorter formula (6.7) prevails.

(iii) In addition to what has been said under (i), we must avoid a possible misunderstanding: The d_p states $|\lambda\rangle^p$ ($\lambda = 1, \ldots, d_p$) in general do not form a representation space. This can be seen in the following simple counterexample: As we will see in Chap. 7, the three functions

$$p_{[x,y,z]} = [x, y, z] \cdot f(|\vec{r}|) \ ,$$

form a three-dimensional representation space of the group O_h. Then, for example,

$$\Psi(\vec{r}) \equiv x f_1(|\vec{r}|) + y f_2(|\vec{r}|) \equiv p_x^1 + p_y^2 \ ,$$

is already of the form (6.7), but the two functions p_x^1, p_y^2 do not form a representation space unless $f_1(|\vec{r}|) = f_2(|\vec{r}|)$.

(iv) We will find a practical way to calculate the components in the expansion (6.7) in the next section. However, in our example of group C_2, we can half-guess it. Given an arbitrary function $\Psi(\vec{r}) = \Psi(x, y, z)$, then

$$\Psi(\vec{r}) = \underbrace{\frac{1}{2}\left[\Psi(x, y, z) + \Psi(-x, -y, z)\right]}_{\equiv \Psi_A(\vec{r})} + \underbrace{\frac{1}{2}\left[\Psi(x, y, z) - \Psi(-x, -y, z)\right]}_{\equiv \Psi_B(\vec{r})} \ .$$

where now the functions $\Psi_A(\vec{r})$ and $\Psi_B(\vec{r})$ have the transformation behavior of the representations Γ^A and Γ^B.

Proof of Equation (6.7) With the elements $a_i \in G$ and $a_1 = E$ we define the g states

$$|\tilde{\Psi}_i\rangle \equiv \hat{U}_{a_i} |\Psi\rangle \ .$$

If the states $|\tilde{\Psi}_i\rangle$ are not orthormal, we orthonormalise them ($|\tilde{\Psi}_i\rangle \to |\Psi_i\rangle$) keeping the first state unchanged ($|\tilde{\Psi}_1\rangle = |\Psi_1\rangle = |\Psi\rangle$). The d-dimensional ($d \leq g$, since the states may be linearly dependent) subspace $\underline{V}^d$ of $\underline{H}$ spanned by the states $|\Psi_i\rangle$ or $|\tilde{\Psi}_1\rangle$ is invariant with respect to all $\hat{U}_a$, because

$$\hat{U}_a |\tilde{\Psi}_i\rangle = \hat{U}_{a \cdot a_i} |\Psi\rangle \in \underline{V}^d \quad \forall i \ .$$

With the results from Sect. 6.1.2, $\underline{V}^d$ is thus a representation space of a representation $\bar{\Gamma}$ with representation matrices

$$\Gamma_{i,j} = \langle \Psi_i | \hat{U}_a | \Psi_j \rangle \ . \tag{6.8}$$

This representation is, in general, reducible,

$$\bar{\Gamma} \sim \sum_{p=1}^{r} n_p \cdot \bar{\Gamma}^p = \tilde{U}^\dagger \cdot \bar{\Gamma} \cdot \tilde{U} \ , \tag{6.9}$$

with a unitary matrix[2]

$$U_{i,j} \equiv U_{i,(p,m,\lambda)} \ ,$$

whose second index is assigned to the irreducible representations ($m = 1, \ldots, n_p$). With this matrix, we define the states

$$|p, m, \lambda\rangle \equiv \sum_i U_{i,(p,m,\lambda)} |\Psi_i\rangle \qquad (m = 1, \ldots, n_p, \lambda = 1, \ldots, d_p) \ .$$

Since $\tilde{U}$ is unitary the inversion of this equation reads

$$|\Psi_i\rangle = \sum_{p,m,\lambda} U^*_{i,(p,m,\lambda)} |p, m, \lambda\rangle \ . \tag{6.10}$$

The states $|p, m, \lambda\rangle$ with fixed p, m and $\lambda = 1, \ldots, d_p$ span an irreducible representation space of G, as can be seen in the following way

$$\hat{U}_a |p, m, \lambda\rangle = \sum_i U_{i,(p,m,\lambda)} \cdot \hat{U}_a |\Psi_i\rangle \ .$$

Since

$$\hat{U}_a |\Psi_i\rangle = \sum_j \Gamma_{j,i}(a) |\Psi_j\rangle \overset{(6.9)}{=} \sum_j \sum_{p',m',\lambda'} \Gamma_{j,i}(a) \cdot U^*_{j,(p',m',\lambda')} |p', m', \lambda'\rangle \ .$$

we find

$$\begin{aligned} \hat{U}_a |p, m, \lambda\rangle \ &= \sum_{p',m',\lambda'} \sum_{i,j} U^*_{j,(p',m',\lambda')} \cdot \Gamma_{j,i}(a) \cdot U_{i,(p,m,\lambda)} |p', m', \lambda'\rangle \\ &\overset{(6.9)}{=} \sum_{\lambda'} \Gamma^p_{\lambda',\lambda} |p, m, \lambda'\rangle \ . \ \surd \end{aligned} \tag{6.11}$$

With (6.10) we can write the state $|\Psi\rangle = |\Psi_1\rangle$ as

$$|\Psi\rangle = \sum_{p,\lambda} \underbrace{\sum_{m=1}^{n_p} U^*_{1,(p,m,\lambda)} |p, m, \lambda\rangle}_{\equiv |\lambda\rangle^p} \ . \tag{6.12}$$

Formally, this creates an expression of the form in (6.7). However, it remains necessary to demonstrate that the state denoted as $|\lambda\rangle^p$ in (6.12) possesses the necessary characteristics. To accomplish this, we must determine the partner functions of $|\lambda\rangle^p$ as

[2] $\tilde{U}$ can be chosen unitary, since $\bar{\Gamma}$ is unitary and $\bar{\Gamma}^p$ can be assumed to be unitary (see Sect. 4.1.1).

$$|\bar{\lambda}\rangle^p \equiv \sum_{m=1}^{n_p} U_{1,(p,m,\lambda)} |p, m, \bar{\lambda}\rangle \ . \tag{6.13}$$

Note that, on the right-hand side of this equation, the index of $\tilde{U}$ is indeed λ, i.e. the value of λ in $|\lambda\rangle^p$ and not $\bar{\lambda}$ which is the label for the partner functions of $|\lambda\rangle^p$. The states $|\bar{\lambda}\rangle$ (of which $|\lambda\rangle^p$ is one for $\bar{\lambda} = \lambda$) indeed form a representation space, because

$$\begin{aligned} \hat{U}_a |\bar{\lambda}\rangle^p &\overset{(6.13)}{=} \sum_{m=1}^{n_p} U_{1,(p,m,\lambda)} \cdot \hat{U}_a |p, m, \bar{\lambda}\rangle \\ &\overset{(6.11)}{=} \sum_{\bar{\lambda}'} \Gamma^p_{\bar{\lambda}',\bar{\lambda}} \cdot U_{1,(p,m,\lambda)} |p, m, \bar{\lambda}'\rangle \overset{(6.13)}{=} \sum_{\bar{\lambda}'} \Gamma^p_{\bar{\lambda}',\bar{\lambda}} |\bar{\lambda}'\rangle^p \quad \surd \ . \end{aligned}$$

Before we look at examples of the development theorem, we will first derive a practical way to determine the components in (6.7) in the following section. This is based on the projection operators introduced by Wigner [1].

6.2 Projection Operators

Let $\bar{\Gamma}^p$ be the d_p-dimensional (unitary) representations of a group G of unitary operators $\hat{U}_a$ $(p = 1, \ldots, r)$. Then, for each p we define the d_p^2 operators

$$\hat{P}^p_{\lambda,\lambda'} \equiv \frac{d_p}{g} \sum_a \left(\Gamma^p_{\lambda,\lambda'}(a)\right)^* \cdot \hat{U}_a \ . \tag{6.14}$$

The following is true

(i) The d_p operators $\hat{P}^p_{\lambda,\lambda}$ are projection operators[3] and applied to an arbitrary state $|\Psi\rangle$ in (6.7), yield exactly the component $|\lambda\rangle^p$.
(ii) For fixed λ, the $d_p - 1$ operators applied to $|\Psi\rangle$ $(\mu \neq \lambda)$ yield the partner functions $|\mu\rangle^p$ of $|\lambda\rangle^p$.

Proof

(i) $\hat{P}^p_{\lambda,\lambda}$ is a projection operator, because

$$\left(\hat{P}^p_{\lambda,\lambda}\right)^\dagger \overset{(6.14)}{=} \frac{d_p}{g} \sum_a \underbrace{\Gamma^p_{\lambda,\lambda}(a)}_{=\left(\Gamma^p_{\lambda,\lambda}(a^{-1})\right)^*} \cdot \underbrace{\hat{U}_a^\dagger}_{=\hat{U}_{a^{-1}}} \overset{(a^{-1} \to a)}{=} \frac{d_p}{g} \sum_a \left(\Gamma^p_{\lambda,\lambda}(a)\right)^* \cdot \hat{U}_a = \hat{P}^p_{\lambda,\lambda} \ ,$$

[3] Recall that a projection operator $\hat{P}$ has the properties $\hat{P}^\dagger = \hat{P}$ and $\hat{P}^2 = \hat{P}$.

and

$$\left(\hat{P}^p_{\lambda,\lambda}\right)^2 = \frac{d_p^2}{g^2}\sum_{a,a'}\left(\Gamma^p_{\lambda,\lambda}(a)\right)^*\cdot\left(\Gamma^p_{\lambda,\lambda}(a')\right)^*\cdot\hat{U}_{a\cdot a'}$$
$$\overset{(b\equiv a\cdot a')}{=}\frac{d_p^2}{g^2}\sum_{a,b}\left(\Gamma^p_{\lambda,\lambda}(a)\right)^*\cdot\left(\Gamma^p_{\lambda,\lambda}(a^{-1}\cdot b)\right)^*\cdot\hat{U}_b\ .$$

Since

$$\left(\Gamma^p_{\lambda,\lambda}(a^{-1}\cdot b)\right)^* = \sum_{\lambda'}\left(\Gamma^p_{\lambda,\lambda'}(a^{-1})\right)^*\cdot\left(\Gamma^p_{\lambda',\lambda}(b)\right)^*\ ,$$

we can evaluate the sum over a with the help of the orthogonality theorem (5.1) and thus it follows that

$$\left(\hat{P}^p_{\lambda,\lambda}\right)^2 = \hat{P}^p_{\lambda,\lambda}\ .$$

It remains to be shown that

$$\hat{P}^p_{\lambda,\lambda}|\Psi\rangle = |\lambda\rangle^p\ ,$$

which will be done together with the proof of statement (ii).

(ii) To prove this statement, we only have to apply $\hat{P}^p_{\mu,\lambda}$ to a general state (6.7)

$$\hat{P}^p_{\mu,\lambda}|\Psi\rangle \overset{(6.7)}{=}\sum_{p',\lambda'}\hat{P}^p_{\mu,\lambda}|\lambda'\rangle^{p'} \overset{(6.14)}{=}\sum_{p',\lambda'}\frac{d_p}{g}\sum_a\left(\Gamma^p_{\mu,\lambda}(a)\right)^*\cdot\hat{U}_a|\lambda'\rangle^{p'}\ . \quad (6.15)$$

With the partner functions $|\mu'\rangle^{p'}$ of $|\lambda'\rangle^{p'}$ we find

$$\hat{U}_a|\lambda'\rangle^{p'} = \sum_{\mu'}\Gamma^p_{\mu',\lambda'}(a)|\mu'\rangle^{p'}\ .$$

If one uses this equation in (6.15) and again the orthogonality theorem (5.1), then it follows

$$\hat{P}^p_{\mu,\lambda}|\Psi\rangle = |\mu\rangle^p\ .\surd$$

The operators $\hat{P}^p_{\lambda,\lambda}$ yield the following straightforward criterion: A state $|\Psi\rangle$ is a member of the λth line of the representation $\bar{\Gamma}^p$ if and only if it satisfies the following condition:

$$\hat{P}^p_{\lambda,\lambda}|\Psi\rangle = |\Psi\rangle\ ,$$

which means that $|\Psi\rangle$ is an eigenvector of $\hat{P}^p_{\lambda,\lambda}$ with an eigenvalue of 1. In order to utilize the operators $\hat{P}^p_{\lambda,\lambda}$, it is necessary to possess the representation matrices $\tilde{\Gamma}(a)$. However, if the goal is only to project the component

$$|\Psi_p\rangle = \sum_{\lambda} |\lambda^p\rangle$$

out of the state (6.7) (rather than a specific state $|\lambda^p\rangle$), an alternative method involving another projection operator can be employed, as demonstrated in Exercise 4. This operator is given by

$$\hat{P}^p \equiv \frac{d_p}{g} \sum_a \left(\chi^p(a)\right)^* \cdot \hat{U}_a \ , \tag{6.16}$$

and only necessitates the use of characters which can be readily found in character tables.

The information that has been presented thus far regarding projection operators should prove adequate for most practical purposes. For additional insights, readers may refer to the seminal text on group theory in physics by Wigner [1].

Example As an example, let us look again at the group C_2. Since both irreducible representations are one-dimensional here, the operators (6.14) and (6.16) are identical and given as

$$\hat{P}^A = \frac{1}{2}\left(\hat{1} + \hat{U}_{\delta_2}\right) \quad , \quad \hat{P}^B = \frac{1}{2}\left(\hat{1} - \hat{U}_{\delta_2}\right) \ . \tag{6.17}$$

They have the expected properties

$$\hat{P}^A \Psi(x, y, z) = \frac{1}{2}\left(\Psi(x, y, z) + \Psi(-x, -y, z)\right) \ ,$$
$$\hat{P}^B \Psi(x, y, z) = \frac{1}{2}\left(\Psi(x, y, z) - \Psi(-x, -y, z)\right) \ ,$$

being even or odd under the two-fold rotation. We will consider more complicated examples after discussing the irreducible representations of point groups in solids in Chap. 7.

6.2.1 *Theorem on the Orthogonality of Representation Spaces*

If $|\lambda\rangle^p$ and $|\lambda'\rangle^{p'}$ belong to the λ th and λ' th row of the representations $\bar{\Gamma}^p$ and $\bar{\Gamma}^{p'}$, then they are orthogonal if $p \neq p'$ or $\lambda \neq \lambda'$.

Proof The proof is the same as in Sect. 6.1.2, and therefore needs not be repeated here.

6.3 Hamiltonians with Symmetries

6.3.1 Reminder: Degeneracies in Quantum Mechanics

Let us provide a brief recapitulation of how the majority of introductory textbooks and lectures on quantum mechanics determine the degeneracy of quantum mechanical spectra:

Assume a physical system is characterized by a Hamiltonian $\hat{H}$. A common approach is to search for a complete set of observables $\hat{O}_i$ $(i = 1, \ldots, m)$ that commute with $\hat{H}$ and with each other. Here, completeness indicates that there are no other observables that cannot be expressed as a function of the $\hat{O}_i$. Subsequently, a unique basis $|n, \alpha_1, \ldots, \alpha_n\rangle$ composed of eigenstates of the observables is established in the Hilbert space,

$$\hat{H}|n, \alpha_1, \ldots, \alpha_n\rangle = E_{n,\alpha_1,\ldots,\alpha_m}|n, \alpha_1, \ldots, \alpha_n\rangle \ ,$$
$$\hat{O}_i|n, \alpha_1, \ldots, \alpha_n\rangle = \alpha_i|n, \alpha_1, \ldots, \alpha_n\rangle \ .$$

To illustrate this concept, let us consider the case of a particle in a rotationally symmetric potential with a Hamiltonian $\hat{H}$. In this scenario, there are two observables that satisfy the aforementioned criteria, namely $\hat{O}_1 = \hat{\vec{L}}^2$ and $\hat{O}_2 = \hat{L}_z$, where $\hat{\vec{L}}$ represents the angular momentum vector operator. The eigenstates and eigenenergies can be expressed as $|n, l, m\rangle$ and $E = E_{n,l}$, respectively, where n, l, and m are quantum numbers and

$$\hat{\vec{L}}^2|n, l, m\rangle = l(l+1)|n, l, m\rangle \quad l = 0, 1, \ldots, \infty \ ,$$
$$\hat{L}_z|n, l, m\rangle = m|n, l, m\rangle \quad m = -l, \ldots, l \ .$$

The eigenvalues of the Hamiltonian in the case of a particle in a rotationally symmetric potential do not depend on the quantum number m, leading to a degeneracy of $(2l + 1)$. However, in this conventional approach, determining the degeneracies of the spectrum and the qualitative properties of the eigenstates require a diagonalization of the Hamiltonian (or at least the angular part as in the example above), which is not feasible for most systems. To obtain insight into the qualitative nature of the spectrum of a Hamiltonian without diagonalizing it, group theory is a very valuable tool.

In quantum mechanics, two types of degeneracies are commonly distinguished: *natural degeneracies* and *accidental degeneracies*. Natural degeneracies are those that are preserved under symmetry-preserving changes of the Hamiltonian, while accidental degeneracies are those that are not. Even small perturbations can break accidental degeneracies. While the distinction between the two types of degeneracy is not precisely defined mathematically, it is a useful concept in physics for understanding the qualitative properties of a Hamiltonian's spectrum. As we shall see in

the following, group theory can only make statements about the natural degeneracies, but these are in practice the most important ones.

6.3.2 Group Theoretical Treatment

As we motivated in Sect. 1.2.3 for single-particle systems, a group of unitary operators $\hat{U}_a$ is called a symmetry group of a Hamiltonian $\hat{H}$ if

$$[\hat{U}_a, \hat{H}] = 0 \quad \forall a \ . \tag{6.18}$$

The group is called a *maximal symmetry group* if it is not a sub-group of another symmetry group of $\hat{H}$. It holds: If $|\Psi_p\rangle$ is an eigenstate of $\hat{H}$,

$$\hat{H}|\Psi_p\rangle = E_p|\Psi_p\rangle \ ,$$

then

$$|\Psi'_p\rangle \equiv \hat{U}_a|\Psi_p\rangle \ ,$$

is obviously also an eigenstate to the the same eigenvalue E_p. The subspace $\underline{V}^p$ to the eigenvalue E_p is therefore invariant subspace with respect to all $\hat{U}_a$. Thus, because of our statement in Sect. 6.1.3 $\underline{V}^p$ is a representation space of G.

6.3.3 Irreducibility Postulate

Let $\underline{V}^p$ be an eigenspace to the eigenvalue E_p of $\hat{H}$ and thus a representation space to each symmetry group of $\hat{H}$. Then it holds that

(i) $\underline{V}^p$ is irreducible with respect to the maximum symmetry group, provided the degeneracy is not accidental;
(ii) With respect to a non-maximal symmetry group $\underline{V}^p$ is, in general, reducible.

In other words, the postulate states that every eigenspace of a Hamiltonian is associated with exactly one irreducible representation of its maximal symmetry group. Therefore, one can classify the eigenstates of a Hamiltonian as $|p, m_p, \lambda_p\rangle$, where

(i) p, as usual, is the index for the irreducible representation;
(ii) $m_p = 0, 1, \ldots, \infty$ numbers the eigenspaces to the same p. In Hilbert spaces of finite dimension, there is, of course, only a finite number of such representation spaces. It can also be $m_p = 0$, i.e. not every irreducible representation has to be realized in the spectrum of a Hamiltonian, as we will see in the case of the point groups in Chap. 7;

(iii) $\lambda_p = 1, \ldots, d_p$ where the dimension of the representation d_p is identical with the degeneracy of the eigenspace. The eigenvalues of a Hamiltonian result solely from the irreducible representations of the symmetry group without having to diagonalize the Hamiltonian.

In the following we will refer to the maximum symmetry group as the symmetry group of $\hat{H}$ for the sake of simplicity and will instead point out explicitly when a point group is not the maximum one.

6.3.4 *Example: A Particle in a One-Dimensional Potential*

We consider the simple text-book example of particle in a one-dimensional potential described by the Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x}) \ ,$$

with a symmetric potential $V(-x) = V(x)$. More complicated examples will be discussed in later chapters. The symmetry group of $\hat{H}$ is $C_i = \{E, I\}$. This is isomorphic to C_2 and therefore has the irreducible representations $\bar{\Gamma}^A$ and $\bar{\Gamma}^B$ whose characters are shown in Table 6.1. With the results of this chapter we find the following:

(i) Concerning the eigenstates we can conclude: Since the representations are one-dimensional, $\hat{H}$ cannot have any degenerate eigenstates. The eigenstates $\Psi^p(x)$ are either symmetric under inversion $x \to -x$ ($p = A$) or antisymmetric ($p = B$).

(ii) The expansion theorem (6.7) says here that every function $\Psi(x)$ can be written as a linear combination of a symmetric and an antisymmetric function

$$\Psi(x) = \underbrace{\frac{1}{2}\left(\Psi(x) + \Psi(-x)\right)}_{\text{symmetric}} + \underbrace{\frac{1}{2}\left(\Psi(x) - \Psi(-x)\right)}_{\text{antisymmetric}} \ . \tag{6.19}$$

(iii) The projection operators that give us the two components in (6.19) are here

$$\hat{P}^A = \frac{1}{2}(1 + I) \quad , \quad \hat{P}^B = \frac{1}{2}(1 - I) \ . \tag{6.20}$$

Because of the isomorphism of the two groups C_i and C_2, the operators (6.20) are of course the same as in (6.17).

6.3.5 Diagonalization of Hamiltonians

In practice, one usually diagonalizes a Hamiltonian $\hat{H}$ by choosing a basis $|\varphi_i\rangle$ and then tries to diagonalize the (in general infinite dimensional) Hamiltonian matrix with the elements

$$H_{i,j} = \langle\varphi_i|\hat{H}|\varphi_j\rangle \ ,$$

(in rare cases) analytically or approximately with numerical techniques. Group theory now helps us to find a suitable basis. Let G be the symmetry group of $\hat{H}$ with the r irreducible representations $\bar{\Gamma}^p$. Then, according to the postulate in Sect. 6.3.3, the Hamiltonian can be written as

$$\hat{H} = \sum_{q,m_q,\lambda_q} E(q,m_q)|q,m_q,\lambda_q\rangle\langle q,m_q,\lambda_q| \ ,$$

with the unknown eigenfunctions $|q,m_q,\lambda_q\rangle$ and eigenvalues $E(q,m_q)$ of $\hat{H}$. We now choose a basis $|\varphi_{p,m,\lambda}\rangle$ of the Hilbert space which consists of orthogonal representation spaces with respect to G with irreducible representations $\bar{\Gamma}^p$ (for example with the projection operators $\hat{P}^p_{\lambda,\lambda}$ introduced in Sect. 6.2). Then, the matrix elements of $\hat{H}$ with respect to this basis has the form

$$\begin{aligned}\langle\varphi_{p,m_p,\lambda_p}|\hat{H}|\varphi_{p',m_{p'},\lambda_{p'}}\rangle &= \sum_{q,m_q,\lambda_q} E(q,m_q)\langle\varphi_{p,m_p,\lambda_p}|q,m_q,\lambda_q\rangle\langle q,m_q,\lambda_q|\varphi_{p',m_{p'},\lambda_{p'}}\rangle \\ &\overset{6.2.1}{=} \delta_{p,p'}\delta_{\lambda_p,\lambda_{p'}} H^{(p,\lambda)}_{m_p,m_{p'}} \ , \end{aligned} \tag{6.21}$$

where we have introduced the matrix $\tilde{H}^{(p,\lambda)}$ with the elements

$$H^{(p,\lambda)}_{m,m'} = \langle\varphi_{p,m,\lambda}|\hat{H}|\varphi_{p,m',\lambda}\rangle \ . \tag{6.22}$$

The diagonalization of $\hat{H}$ is thus reduced to that of the matrices $\tilde{H}^{(p,\lambda)}$. With (6.21), the maximum possible block diagonality due to the symmetry is established. In numerical practice, of course, the procedure introduced here is only worthwhile if $\tilde{H}^{(p,\lambda)}$ can be determined analytically. Applied to the one-dimensional potential in Sect. 6.3.4, (6.22) reproduces our finding from above that one can diagonalize the Hamiltonian independently in the space of symmetric and antisymmetric wave functions.

Finally, the calculation of the matrix element (6.22) is made even easier by the fact that it is independent of λ, i.e.

$$H^{(p,\lambda)}_{m,m'} = H^p_{m,m'} \ . \tag{6.23}$$

Proof Using (6.18) we find

$$\hat{H} = \hat{U}_a \cdot \hat{H} \cdot \hat{U}_a^\dagger \ ,$$

which we substitute into the matrix element (6.22),

$$H_{m,m'}^{(p,\lambda)} = \langle \varphi_{p,m,\lambda} | \hat{H} | \varphi_{p,m',\lambda} \rangle = \langle \varphi_{p,m,\lambda} | \hat{U}_a \cdot \hat{H} \cdot \hat{U}_a^\dagger | \varphi_{p,m',\lambda} \rangle \tag{6.24}$$
$$\overset{(6.1)/(6.21)}{=} \sum_{\lambda'} \Gamma_{\lambda',\lambda}(a) \left(\Gamma_{\lambda',\lambda}(a)\right)^* \langle \varphi_{p,m,\lambda'} | \hat{H} | \varphi_{p,m',\lambda'} \rangle \ .$$

Since the left-hand side does not depend on a, the same must be true for the right-hand side. We can now sum over a on both sides in (6.24), which then leads to

$$\langle \varphi_{p,m,\lambda} | \hat{H} | \varphi_{p,m',\lambda} \rangle = \frac{1}{d_p} \sum_{\lambda'} \langle \varphi_{p,m,\lambda'} | \hat{H} | \varphi_{p,m',\lambda'} \rangle \ .$$

where we used the orthogonality theorem (5.2). Since the right-hand side is independent of λ, the assertion follows. $\surd$

Example As an example, we consider a rectangular 'molecule' with one orbital per site on which a single quantum mechanical particle is located (see Fig. 6.2). The Hamiltonian contains a hopping t, t' to the nearest neighbors which in first quantization reads

$$\hat{H} = \sum_{i,j=1}^{4} t_{i,j} |i\rangle\langle j| \ ,$$

where the values of $t_{i,j}$ are specified in Fig. 6.2. In matrix form the Hamiltonian is given as

$$\tilde{H} = \begin{pmatrix} 0 & t' & 0 & t \\ t' & 0 & t & 0 \\ 0 & t & 0 & t' \\ t & 0 & t' & 0 \end{pmatrix} \ .$$

There are obviously 4 symmetry operations, besides the one-element a rotation δ_2 around the z-axis with angle π as well as the two mirror planes σ_1 ($x = 0$) and σ_2

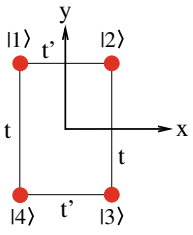

Fig. 6.2 A rectangular 'molecule' with one orbital per site

Table 6.2 Character table of the group C_{2v}

C_{2v}	E	δ_2	σ_1	σ_2
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

($y = 0$). Therefore, the symmetry group of the molecule is C_{2v} (see Chap. 3). It has 4 (of course one-dimensional) irreducible representations, which are shown in the character Table 6.2. To use (6.21), we need a basis of representation spaces. We can determine it with the projection operators (6.16). In this case, it is sufficient to take only one of the four states $|i\rangle$ and apply the 4 operators $\hat{P}^p$ to it,

$$\begin{aligned}
\hat{P}^{A_1}|1\rangle &\overset{6.2.1}{=} \frac{1}{4}\left(\hat{U}_E|1\rangle + \hat{U}_{\delta_2}|1\rangle + \hat{U}_{\sigma_1}|1\rangle + \hat{U}_{\sigma_2}|1\rangle\right) \\
&= \frac{1}{4}\left(|1\rangle + |4\rangle + |2\rangle + |3\rangle\right) \equiv \sqrt{4}|\Psi_{A_1}\rangle\ , \\
\hat{P}^{A_2}|1\rangle &= \frac{1}{4}\left(|1\rangle + |4\rangle - |2\rangle - |3\rangle\right) \equiv \sqrt{4}|\Psi_{A_2}\rangle\ , \\
\hat{P}^{B_1}|1\rangle &= \frac{1}{4}\left(|1\rangle - |4\rangle + |2\rangle - |3\rangle\right) \equiv \sqrt{4}|\Psi_{B_1}\rangle\ , \\
\hat{P}^{B_2}|1\rangle &= \frac{1}{4}\left(|1\rangle - |4\rangle - |2\rangle + |3\rangle\right) \equiv \sqrt{4}|\Psi_{B_2}\rangle\ .
\end{aligned}$$

where the factor $\sqrt{4}$ has been introduced to normalize the 4 states $|\Psi_p\rangle$. These 4 states are orthogonal and therefore form a base of the Hilbert space. Since they belong to different representations, $\hat{H}$ must be diagonal in this basis, i.e. the matrices (6.22) here are one-dimensional with respect to $m_p, m_{p'}$,

$$\begin{aligned}
\tilde{H}' &= \begin{pmatrix}
\langle\Psi_{A_1}|\hat{H}|\Psi_{A_1}\rangle & 0 & 0 & 0 \\
0 & \langle\Psi_{A_2}|\hat{H}|\Psi_{A_2}\rangle & 0 & 0 \\
0 & 0 & \langle\Psi_{B_1}|\hat{H}|\Psi_{B_1}\rangle & 0 \\
0 & 0 & 0 & \langle\Psi_{B_2}|\hat{H}|\Psi_{B_2}\rangle
\end{pmatrix} \\
&= \begin{pmatrix}
t+t' & 0 & 0 & 0 \\
0 & t-t' & 0 & 0 \\
0 & 0 & -t+t' & 0 \\
0 & 0 & 0 & -t-t'\rangle
\end{pmatrix}\ .
\end{aligned}$$

In this simple case, we have therefore succeeded in diagonalizing a Hamiltonian just by choosing a proper basis based on group theory.

Exercises

1. Using the operators $\hat{P}^p_{\lambda,\lambda}$, determine the expansion of the form (6.7) for the state

$$\Psi(\vec{r}) = x \cdot y \cdot f(|\vec{r}|) \ ,$$

with respect to the group C_3 (with the z-axis as the symmetry axis).

2. In the following, we consider molecules with one orbital per lattice site described by a Hamiltonian of the form

$$\hat{H} = \sum_{i \neq j} t_{i,j} |i\rangle\langle j| \ ,$$

with hopping parameters as indicated in Fig. 6.3.

(a) First, consider the triangular molecule in Fig. 6.3a. Determine a basis of orthogonal representation spaces to the symmetry group C_{3v} of the Hilbert space and diagonalize the Hamiltonian with it.
(b) Solve the same problem for the molecule in Fig. 6.3b.
(c) What is the Hamiltonian matrix when you apply the procedure to a (admittedly artificial) molecule with L triangles, that are arranged in the same way?

Note: In addition to the character table of C_{3v}, which is the same as that of D_3 in Table 5.1 (with $3\delta_2$ replaced by $3\sigma_v$) use the following two-dimensional matrices of the representation E:

$$\tilde{\Gamma}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \tilde{\Gamma}(\delta_3)^* = \begin{pmatrix} \omega & 0 \\ 0 & \omega^2 \end{pmatrix}, \tilde{\Gamma}(\delta_3^2)^* = \begin{pmatrix} \omega^2 & 0 \\ 0 & \omega \end{pmatrix} \ , \quad \left(\omega = e^{-2\pi \mathrm{i}/3}\right)$$
$$\tilde{\Gamma}(\sigma_1) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \tilde{\Gamma}(\sigma_2)^* = \begin{pmatrix} 0 & \omega^2 \\ \omega & 0 \end{pmatrix}, \tilde{\Gamma}(\sigma_3)^* = \begin{pmatrix} 0 & \omega \\ \omega^2 & 0 \end{pmatrix} \ .$$

3. Show that the following holds for the projection operators $\hat{P}^p_{\lambda,\lambda}$

$$\hat{P}^p_{\lambda,\lambda} \cdot \hat{P}^{p'}_{\lambda',\lambda'} = \delta_{p,p'} \delta_{\lambda,\lambda'} \hat{P}^p_{\lambda,\lambda} \ .$$

4. We consider the operator $\hat{P}^p$, defined in (6.16).

(a) Show that $\hat{P}^p$ is a projection operator.
(b) Show that, if applied to a general state (6.7), it projects out the state

$$|\Psi_p\rangle = \sum_{\lambda} |\lambda\rangle^p \ .$$

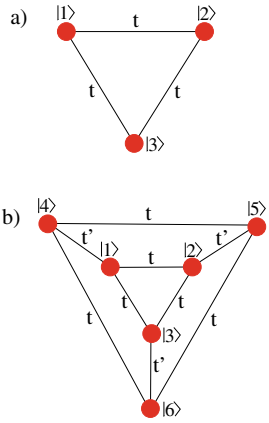

Fig. 6.3 The molecules considered in Exercise 2

Reference

1. Eugene Wigner, Group Theory: And its Application to the Quantum Mechanics of Atomic Spectra, Academic Press, 1936

Chapter 7
Irreducible Representations of the Point Groups in Solids

In this chapter, our focus returns to the irreducible representations of the point groups. Character tables, which can be easily found in various references off- or online, provide not only the familiar information on the characters, but also examples of representation functions. The reason for this will be discussed in Sect. 7.1. Since character tables of the 32 point groups in solids are widely available, we will not reproduce them extensively in this book. Instead, we will provide only the character tables that are needed in the main text or in exercises. In Sect. 7.2, we examine the well-known example of a particle confined in a cube-shaped box potential. In this system, one might expect to find eigenspaces that correspond to the irreducible representations of the group O_h. However, this is not the case, and we will provide an explanation that may help the reader to better understand the irreducibility postulate in Sect. 6.3.3.

7.1 Character Table with Representation Functions

So far, we have mainly focused on simple point groups that have one-dimensional representations, with all necessary information included in their character tables. For non-Abelian groups, however, the character tables may not be sufficient, because one requires the explicit representation matrices in applications.[1] In the literature, this information is usually conveyed in a different way, namely by presenting examples of representation spaces in the character table. Table 7.1 displays the extended character table for the largest point group in solids, O_H, which includes examples of representation spaces alongside the characters. These spaces provide a more intuitive alternative to the representation matrices, and in principle, we can determine

[1] See Exercise 5.2.3 of Chap. 5, where we show that not all irreducible representations are one-dimensional in the case of non-Abelian groups.

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https://doi.org/10.1007/978-3-031-55268-7_7

Table 7.1 Character table of the group O_H

O_H			E	$6C_4$	$3C_4^2$	$8C_3$	$6C_2'$	I	$3\sigma_h$	$6\sigma_d$	$8S_6$	$6S_4$
$x^2+y^2+z^2=r^2$	xyz	A_{1g}	1	1	1	1	1	1	1	1	1	1
		A_{2g}	1	−1	1	1	−1	1	1	−1	1	−1
		A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1
		A_{2u}	1	−1	1	1	−1	−1	−1	1	−1	1
$(x^2-y^2, 3z^2-r^2)$		E_g	2	0	2	−1	0	2	2	0	−1	0
		E_u	2	0	2	−1	0	2	−2	0	1	0
		T_{1g}	3	1	−1	0	−1	3	−1	−1	0	1
(zx, yz, xy)	(x, y, z)	T_{2g}	3	−1	−1	0	1	3	−1	1	0	−1
	$(x(z^2-y^2), y(z^2-x^2), z(x^2-y^2))$	T_{1u}	3	1	−1	0	−1	−3	1	1	0	−1
		T_{2u}	3	−1	−1	0	1	−3	1	−1	0	1

the representation matrices from the representation functions using (6.8).[2] Let us examine this table in greater detail.

(i) We have only provided representation functions that are linear, quadratic, or cubic in terms of x, y, and z. Higher-order functions are required for other representations. As explained later in Chap. 8, the linear, quadratic or cubic functions are applicable to atoms with filled shells of s, p, d or f orbitals. Orders beyond three are usually not relevant in solid-state physics. For completeness, we also give the missing representation functions of orders $3-6$ in x, y, z:

$$A_{2u} : xyz \ , \tag{7.1}$$
$$A_{2g} : x^4(y^2-z^2)+y^4(z^2-x^2)+z^4(x^2-y^2) \ ,$$
$$A_{1u} : xyz\left[x^4(y^2-z^2)+y^4(z^2-x^2)+z^4(x^2-y^2)\right] \ ,$$
$$E_u : xyz\left[(x^2-y^2, 3z^2-r^2)\right] \ ,$$
$$T_{1g} : xy(x^2-y^2), xz(x^2-z^2), yz(y^2-z^2) \ . \tag{7.2}$$

(ii) A convention has been established for the naming of representations:

- One-dimensional representations are labeled as A or B. The difference between A and B denotes the positive or negative character of proper rotations around the main symmetry axis.
- Two- and three-dimensional representations are denoted by E and T, respectively.

[2] As an alternative, one can find all the representation matrices for the 32 point groups on https://www.cryst.ehu.es/. Unlike the customary practice in this book, we provide this specific webpage as it is, to the best of the author's knowledge, the only source that provides all the representation matrices not only for the point groups, but also for other groups.

Table 7.2 Character table of the group C_4

C_4			E	C_4	$C_4^2 = C_2$	C_4^3
$x^2 + y^2, z^2$	z	A	1	1	1	1
$x^2 - y^2, xy$		B	1	-1	1	-1
(zx, zy)	(x, y)	E	$\left\{\begin{matrix}1\\1\end{matrix}\right.$	$\begin{matrix}\mathrm{i}\\-\mathrm{i}\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\left.\begin{matrix}-\mathrm{i}\\\mathrm{i}\end{matrix}\right\}$

- If $I \in G$, the subscript g or u indicates whether the representation is symmetric or antisymmetric under inversion.[3]
- Representations such as A' and A'' differ in their symmetry or antisymmetry relative to the mirror plane perpendicular to the main symmetry axis.[2]

(iii) When dealing with groups that have complex-valued characters, it is necessary to analyze their character tables more closely. For instance, consider the group C_4, whose character table is presented in Table 7.2. This group is Abelian, and therefore its four irreducible representations are one-dimensional. However, in accordance with the literature, the character table shows two representations with complex characters that are denoted as two-dimensional. Here we explain why: the functions

$$p_{[x,y]} \equiv f(|\mathbf{r}|)[x, y] \,,$$

define a two-dimensional representation space of C_4 with the representation matrices

$$\tilde{\Gamma}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad , \quad \tilde{\Gamma}(C_4) = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \quad ,$$
$$\tilde{\Gamma}(C_2) = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \quad , \quad \tilde{\Gamma}(C_4^3) = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \quad .$$

These representation matrices, however, are reducible and can be diagonalized via the transformation

$$\Psi_+ \equiv p_x + \mathrm{i} p_y \quad , \quad \Psi_- \equiv p_x - \mathrm{i} p_y \,.$$

In this basis, the representation matrices are

$$\tilde{\Gamma}'(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad , \quad \tilde{\Gamma}'(C_4) = \begin{pmatrix} \mathrm{i} & 0 \\ 0 & \mathrm{i} \end{pmatrix} \quad ,$$
$$\tilde{\Gamma}'(C_2) = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \quad , \quad \tilde{\Gamma}'(C_4^3) = \begin{pmatrix} -\mathrm{i} & 0 \\ 0 & \mathrm{i} \end{pmatrix} \quad .$$

[3] In Exercise 5.2.3 of Chap. 5 we show that all representation functions must have one of the two properties.

These are exactly the two (conjugate complex) one-dimensional representations that we find in the character Table 7.2.
A Hamiltonian in the two-dimensional subspace of p_x and p_y that leads to non-degenerate eigenstates is

$$\hat{H} = \varepsilon \left(|p_x\rangle\langle p_x| + |p_y\rangle\langle p_y| \right) + \mathrm{i}\Omega \left(|p_x\rangle\langle p_y| - |p_y\rangle\langle p_x| \right) , \tag{7.3}$$

with $\Omega \in \mathbb{R}$. The symmetry group of $\hat{H}$ is still C_4, as shown in Exercise 1, and the eigenstates are $\Psi_\pm$ with eigenvalues

$$E_\pm = \varepsilon \pm \Omega .$$

Hence, in accordance with our group theoretic expectation, the two energies are not degenerate. However, in physics, one-particle Hamiltonians

$$\hat{H}_{\mathrm{sp}} = -\frac{\hbar^2}{2m}\Delta + V(\mathbf{r}) ,$$

are real, which means that the matrix element

$$\langle p_x | \hat{H}_{\mathrm{sp}} | p_y \rangle ,$$

must be real too. This implies that $\Delta = 0$ in $\hat{H}$, leading to a twofold degeneracy that would not be expected from group theory. Therefore, in most character tables (particularly in physics), it is assumed that Hamiltonians are real, and the complex representations are denoted as two-dimensional.
Mathematically, the fact that $\hat{H}_{\mathrm{sp}}$ is real implies that it commutes with the *conjugation operator* $\hat{K}$, which is defined as follows:

$$\hat{K}\,\Psi(\mathbf{r}) = \Psi(\mathbf{r})^* .$$

Since the operator $\hat{K}$ is not unitary but anti-unitary,

$$\langle \hat{K}\Psi_1 | \hat{K}\Psi_2 \rangle = \langle \Psi_2 | \Psi_1 \rangle ,$$

we cannot incorporate it directly into our previous representation theory. Wigner's book (see footnote 1 in Chap. 6) provides a discussion on how to solve this problem. However, for all the applications in this book, we do not need to worry about the issue.

7.2 Example: A Particle in a Cubic Box

To discuss the eigensystem of a system belonging to the point group O_h, let us examine the case of a quantum mechanical particle confined in a cubic box with impenetrable potential walls. This particular system is usually covered in introductory quantum mechanics lectures, and its Hamiltonian can be expressed as follows

$$\hat{H} = \sum_{i=1}^{3} \hat{H}_i \ , \tag{7.4}$$

with

$$\hat{H}_i = \frac{\hat{p}_i^2}{2m} + V(\hat{x}_i) \ ,$$

and the potential (see Fig. 7.1)

$$V(x) = \begin{cases} 0 & \text{if } |x| \leq a \\ \infty & \text{if } |x| > a \end{cases} \ .$$

To solve the eigenvalue problem

$$\hat{H}\Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \ , \tag{7.5}$$

one uses the product Ansatz

$$\Psi_{n_1,n_2,n_3}(\mathbf{r}) \equiv \prod_{i=1}^{3} \Psi_{n_i}(x_i) \ ,$$

which, inserted into (7.5), yields the three decoupled equations

$$\hat{H}_i \Psi_{n_i}(x_i) = E_{n_i} \Psi_{n_i}(x_i) \ .$$

These one-dimensional eigenvalue problems (with the boundary conditions $\Psi_{n_i}(\pm a) = 0$) are probably solved in all textbooks on quantum mechanics, and lead to the eigenstates ($n = 1, 2, \ldots$)

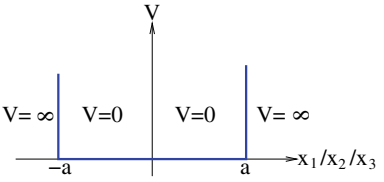

Fig. 7.1 Potential of a quantum mechanical particle in a cubic box

$$\Psi_n(x) = \begin{cases} \cos\left(\frac{\pi}{2a}nx\right) & \text{for odd } n \\ \sin\left(\frac{\pi}{2a}nx\right) & \text{for even } n \end{cases} ,$$

and eigenvalues

$$E_{n_1,n_2,n_3} = \alpha(n_1^2 + n_2^2 + n_3^2) \qquad \left(\alpha = \frac{\hbar^2\pi^2}{8ma^2}\right) .$$

In the following, we consider the eigenspaces of lowest energy and try to find the corresponding irreducible representations with the help of Table 7.1 and maybe (7.1) and (7.2):

(i) Ground state, $E = 3\alpha$ ($n_i = 1$):

$$\Psi_{1,1,1}(\mathbf{r}) \sim \cos(x_1)\cos(x_2)\cos(x_3) \qquad \left(\frac{\pi}{2a} \equiv 1\right).$$

This function obviously transforms like $x^2 + y^2 + z^2$ and therefore belongs to the irreducible representation A_{1g}.

(ii) First excited states, $E = 6\alpha$:

$$\Psi_{1,1,2}(\mathbf{r}) \sim \cos(x_1)\cos(x_2)\sin(2x_3) , \tag{7.6}$$
$$\Psi_{1,2,1}(\mathbf{r}) \sim \cos(x_1)\sin(2x_2)\cos(x_3) ,$$
$$\Psi_{2,1,1}(\mathbf{r}) \sim \sin(2x_1)\cos(x_2)\cos(x_3) . \tag{7.7}$$

The functions exhibit a transformation similar to that of the irreducible representation T_{1u}. This can be seen from the fact that, in T_{1u}, only one of the three spatial components x_i is distinguished, while the other two have a comparable transformation behavior (unlike in T_{2u}). For those who find this explanation insufficient, we provide a more mathematical substantiation in Exercise 2. There we show that the representation E_g appears in the space of the third excited states. The same method could be used to show mathematically that (7.6) and (7.7) belong to the representation T_{1u}.

(iii) Second excited states, $E = 9\alpha$:

$$\Psi_{1,2,2}(\mathbf{r}) \sim \cos(x_1)\sin(2x_2)\sin(2x_3) ,$$
$$\Psi_{2,2,1}(\mathbf{r}) \sim \sin(2x_1)\sin(2x_2)\cos(x_3) ,$$
$$\Psi_{2,1,2}(\mathbf{r}) \sim \sin(2x_1)\cos(x_2)\sin(2x_3) .$$

These functions transform like those of the irreducible representation T_{1g}.

(iv) Third excited states, $E = 11\alpha$:

$$\Psi_{1,1,3}(\mathbf{r}) \sim \cos(x_1)\cos(x_2)\cos(3x_3) \ , \tag{7.8}$$
$$\Psi_{1,3,1}(\mathbf{r}) \sim \cos(x_1)\cos(3x_2)\cos(x_3) \ , \tag{7.9}$$
$$\Psi_{3,1,1}(\mathbf{r}) \sim \cos(3x_1)\cos(x_2)\cos(x_3) \ . \tag{7.10}$$

For this degenerate space, we do not find a corresponding irreducible representation in Table 7.1 or in (7.1) and (7.2). This means that, if the postulate 6.3.3 is correct,

(a) the eigenspace $\underline{V}^{[1,1,3]}$ must be reducible with respect to O_h, and
(b) O_h cannot be the maximum symmetry group of the Hamiltonian (7.4).

We start with point (a) by introducing the basis transformation

$$\Psi_1^{[1,1,3]} \equiv \frac{1}{\sqrt{3}}(\Psi_{3,1,1} + \Psi_{1,3,1} + \Psi_{1,1,3}) \ , \tag{7.11}$$
$$\Psi_2^{[1,1,3]} \equiv \frac{1}{\sqrt{2}}(\Psi_{3,1,1} - \Psi_{1,3,1}) \ , \tag{7.12}$$
$$\Psi_3^{[1,1,3]} \equiv \frac{1}{\sqrt{6}}(2\Psi_{1,1,3} - \Psi_{1,3,1} - \Psi_{3,1,1}) \ . \tag{7.13}$$

It is easy to see that $\Psi_1^{[1,1,3]}$ is another representation function of A_{1g}, i.e.

$$\hat{U}_a \Psi_1^{[1,1,3]} = \Psi_1^{[1,1,3]} \quad \forall a \in G \ .$$

The states $\Psi_2^{[1,1,2]}$ and $\Psi_3^{[1,1,3]}$ constitute a representation space for the representation E_g, transforming like $x^2 - y^2$ and $3z^2 - r^2$ under symmetry operations (see Exercise 2).

If the symmetry group O_h is not the maximal symmetry group of the Hamiltonian (7.4), it must commute with other unitary operators. These operators can be readily determined since $\hat{H}$ commutes with all three $\hat{H}_i$. Therefore, it also commutes with the unitary operators

$$\hat{U}_i(\alpha) \equiv \exp(\mathrm{i}\alpha \hat{H}_i) \ , \tag{7.14}$$

where $\alpha \in \mathbb{R}$.[4] The mathematical definition of $\hat{U}_i(\alpha)$ is somewhat problematic, since $V(x) = \infty$ for $|x| > a$. However, the additional symmetries (7.14) exist for every Hamiltonian of the form (7.4), including a potential whose value is v_w but not infinite for $|x| > a$. In this case, the higher degeneracy will not disappear in the limit $v_w \to \infty$.

[4] The effects of these additional symmetries are discussed in more detail in arXiv:1310.5136 and Am. J. Phys. 65 (1087).

In Exercise 3 of Chap. 8 we convince ourselves that the splitting found here also results if we add a potential to the Hamiltonian with which the system then indeed has the maximum symmetry group O_h.

Exercises

1. Show that C_4 is a symmetry group of the Hamiltonian (7.3).
2. Show that the two eigenfunctions (7.12) and (7.13) belong to the representation E_g.
   Hint: It is sufficient to show that the transformations of the group in this two-dimensional subspace lead to characters corresponding to those in Table 7.1.
3. Consider a particle in a box potential

$$V(\mathbf{r}) = V(x, y, z) = \begin{cases} 0 & x, y \in [-a, a] \text{ and } z \in [-b, b] \\ \infty & \text{else} \end{cases} .$$

   The dimensions a, b are chosen such that the energy eigenvalues are of the form

$$E(n_1, n_2, n_3) = \alpha(n_1^2 + n_2^2 + \pi n_3^2) .$$

   Find out if the five lowest energy eigenspaces are irreducible representation spaces of the symmetry group D_{4h} of the system (character tables of the group D_{4h} can be readily found online). If not, determine their irreducible subspaces with respect to D_{4h}.
4. We look again at the particle in the cube-shaped box and add a potential of the form (see Sect. 7.2)

$$V'(x) = \begin{cases} -U & \text{if } |x| \leq \frac{1}{2} \\ 0 & \text{if } |x| > \frac{1}{2} \end{cases}$$

   to it. What qualitative form does the Hamiltonian matrix have in the 7-dimensional subspace of the first three eigenspaces which we found without this additional potential in Sect. 7.2?
5. Show that the three-dimensional rotation matrices of the group O_h correspond to the irreducible representation T_{1u} of this group.

Chapter 8
Group Theory in Stationary Perturbation Theory Calculations

This chapter focuses on the usefulness of group theory in the stationary perturbation theory. In Sect. 8.1, we revisit Rayleigh-Schrödinger perturbation theory. The concept of the subduced representation and its reduction are relevant for degenerate perturbation theory, which we discuss in Sects. 8.2 and 8.3. In Sect. 8.4, we explore an application crucial for solid-state physics: the splitting of atomic spectra in crystal fields. Finally, in Sect. 8.5, we investigate how to analyze matrix elements in perturbation theory with group theoretical means.

8.1 Reminder: Rayleigh-Schrödinger Perturbation Theory

Rayleigh-Schrödinger perturbation theory is a common tool in quantum mechanics and is therefore included in most textbooks on the subject. Thus we will only provide a brief summary of the essential findings regarding degenerate and non-degenerate perturbation theory. In general, perturbation theory deals with Hamiltonians of the form

$$\hat{H} = \hat{H}_0 + \hat{V} \ ,$$

whose eigenvalue problem

$$\hat{H}|n\rangle = E_n|n\rangle \ ,$$

we want to solve approximately, whereby the eigenvalue problem

$$\hat{H}_0|n\rangle_0 = E_n^0|n\rangle_0 \ ,$$

is assumed to be solved. Then we distinguish two cases:

(i) The eigenvalue E_n^0 is non-degenerate. Then, the eigenstates $|n\rangle$ and eigenvalues E_n in the leading order in $\hat{V}$ are given by

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J. Bünemann, *Group Theory in Physics*, Undergraduate Lecture Notes in Physics,
https://doi.org/10.1007/978-3-031-55268-7_8

$$E_n = E_n^0 + {}_0\langle n|\hat{V}|n\rangle_0 + \sum_{n'(\neq n)} \frac{|{}_0\langle n|\hat{V}|n'\rangle_0|^2}{E_n^0 - E_{n'}^0} + \mathcal{O}(\hat{V}^3) \,, \tag{8.1}$$

$$|n\rangle = |n\rangle_0 + \sum_{n'(\neq n)} \frac{{}_0\langle n'|\hat{V}|n\rangle_0}{E_n^0 - E_{n'}^0} |n'\rangle_0 + \mathcal{O}(\hat{V}^2) \,. \tag{8.2}$$

The question arising here is how to simplify the calculation of the matrix elements ${}_0\langle n|\hat{V}|n'\rangle_0$ and to identify those that are zero, using group theory.[1] There are two cases where group theory can be particularly helpful in analyzing such matrix elements:

- When the symmetry group of $\hat{V}$ is a sub-group of the symmetry group of $\hat{H}_0$, with the special case where the groups are identical. This case is discussed in Sect. 8.5.
- When $\hat{V}$ is the component of a tensor operator (with the special case of a vector operator). In this case, the Wigner-Eckhart theorem can be used to analyze matrix elements. We consider this theorem only in Chap. 10, since we first need to introduce and discuss the tensor operators in Chap. 9.

(ii) The eigenvalue E_n^0 is degenerate, so there are $d > 1$ eigenvectors with the same eigenvalue E_n^0,

$$\hat{H}_0|n_i\rangle_0 = E_n^0|n_i\rangle_0 \quad (\text{for } \; n_i = 1, \ldots, d) \,.$$

The energy splitting in first order then results from the diagonalization of the matrix $\tilde{V}$ with the elements

$$V_{i,j} = {}_0\langle n_i|\hat{V}|n_j\rangle_0 \,.$$

The eigenfunctions $|\alpha\rangle$ of $\hat{V}$ with the eigenvalues ΔE_α are called *adapted zeroth order eigenfunctions* with the energies

$$E_\alpha = E_n^0 + \Delta E_\alpha \,.$$

The group-theoretical question that arises here, and which we will analyze in this chapter, is which splittings of the spectra are to be expected based solely on the symmetry groups of $\hat{H}$ and $\hat{H}_0$.
If the energies are completely split in the 0th order, one can use the expressions (8.1), (8.2) of the non-degenerate perturbation theory with the states $|\alpha\rangle$ and energies E_α to determine higher orders. In practice, however, this is almost never the case and the situation becomes more complex. One then needs to resort

[1] The reader is reminded that these questions cannot be investigated systematically without the group theory. In the standard examples in textbooks on quantum mechanics, one uses special methods which can only be employed in these individual cases.

to projection operator techniques, as outlined in the textbook by Messiah.[2] Group theory may also be useful in such calculations, however, this topic is outside the scope of this textbook.

Let G and G_0 be the symmetry groups of $\hat{H}$ and $\hat{H}_0$. Then, the most important case physically is that G is a sub-group of G_0 (with the special case $G = G_0$). Of course, we could also construct other situations:

(i) G_0 is a real sub-group of G, for example for a quantum-mechanical particle in three dimensions with the Hamiltonian

$$\hat{H}_0 = \frac{\hat{\vec{p}}^2}{2m} + \alpha(\hat{x}^2 + \hat{y}^2) \quad , \quad \hat{V} = \alpha\hat{z}^2 \, .$$

(ii) There are elements $a \in G_0, b \in G$ for which $a \notin G, b \notin G_0$, e.g.

$$\hat{H}_0 = \frac{\hat{\vec{p}}^2}{2m} + \alpha(\hat{x}^2 + \hat{y}^2) \quad , \quad \hat{V} = \alpha(\hat{z}^2 - \hat{x}^2) \, .$$

Such artificial cases, however, are (if at all) only of academic interest.

8.2 Subduced Representations

Let us revisit the concept of subduced representations, which we had already introduced in Exercise 5.2.3 of Chap. 5. Suppose we have a sub-group G of G_0 and a representation $\bar{\Gamma}$ of G_0.[3] The matrix group of representation matrices $\tilde{\Gamma}(a)$ with $a \in G$ is also a representation of G, which is called the *subduced representation* $\bar{\Gamma}^{(\mathrm{s})}$. Even if $\bar{\Gamma}$ is irreducible with respect to G_0, $\bar{\Gamma}^{(\mathrm{s})}$ is generally reducible with respect to G. In this case, there is a reduction of the form

$$\bar{\Gamma}^{(\mathrm{s})} = \sum_{p=1}^{r} n_p \cdot \bar{\Gamma}^p \, ,$$

where the $\bar{\Gamma}^p$ are the irreducible representations of G, and the numbers n_p can be determined using (5.23), as is always the case.

For instance, let us examine the groups $G_0 = D_3$ and $G = C_2$, whose characters are given in Table 8.1. The irreducible representation of D_3, labeled as E, is a

[2] A. Messiah, *Quantum Mechanics*, Dover, 1999.

[3] We change the notation for groups and their sub-groups in this discussion, as G_0/G will represent the symmetry groups of $\hat{H}_0/\hat{H}$, which is a well-established notation in the literature.

Table 8.1 The character tables of the point groups D_3 and C_2

D_3			E	$2C_3$	$3C_2$
x^2+y^2, z^2		A_1	1	1	1
	z	A_2	1	1	1
(zx, yz) (x^2-y^2, xy)	(x, y)	E	2	−1	0

C_2			E	$2C_2$
x^2, y^2, z^2, xy	z	A	1	1
zx, yz	x, y	B	1	−1

Table 8.2 Correlation table for the group O_h and its largest sub-groups

O_h	O	T_d	T_h	D_{4h}	D_{3d}
A_{1g}	A_1	A_1	A_g	A_{1g}	A_{1g}
A_{2g}	A_2	A_2	A_g	B_{1g}	A_{2g}
A_{1u}	A_1	A_2	A_u	A_{1u}	A_{1u}
A_{2u}	A_2	A_1	A_u	B_{1u}	A_{2u}
E_g	E	E	E_g	$A_{1g} \oplus B_{1g}$	E_g
E_u	E	E	E_u	$A_{1u} \oplus B_{1u}$	E_u
T_{1g}	T_1	T_1	T_g	$A_{2g} \oplus E_g$	$A_{2g} \oplus E_g$
T_{2g}	T_2	T_2	T_g	$B_{2g} \oplus E_g$	$A_{1g} \oplus E_g$
T_{1u}	T_1	T_2	T_u	$A_{2u} \oplus E_u$	$A_{2u} \oplus E_u$
T_{2u}	T_2	T_1	T_u	$B_{2u} \oplus E_u$	$A_{1u} \oplus E_u$

subduced representation concerning C_2, but it is reducible. The outcome of this subduction is given as

$$n_A = \frac{1}{2}\Big(\underbrace{2}_{=(\chi_E^E)^*}\cdot\underbrace{1}_{=\chi_E^{(s)}} + \underbrace{0}_{=(\chi_{C_2}^E)^*}\cdot\underbrace{1}_{=\chi_{C_2}^{(s)}}\Big) = 1\,,$$

$$n_B = \frac{1}{2}(2\cdot 1 - 0\cdot 1) = 1\,,$$

i.e.

$$\bar{\Gamma}_E^{(s)} = \bar{\Gamma}^A \oplus \bar{\Gamma}^B\,.$$

Correlation tables display the reductions of subduced representations. As an illustration, we demonstrate the reductions of subduced representations for certain sub-groups of O_h in Table 8.2 with $G_0 = O_h$. All other correlation tables can be readily found online.

8.3 Degenerate Perturbation Theory

In the first order of the perturbation theory, a degenerate representation space $\underline{V}^p$ (of a representation $\bar{\Gamma}^p$) of $\hat{H}_0$ is given as[4]

$$\underline{V}^p = \underline{\tilde{V}}^{p_1} \oplus \underline{\tilde{V}}^{p_2} \oplus \dots \,, \tag{8.3}$$

where the $\underline{\tilde{V}}^{p_i}$ must be irreducible representation spaces to the symmetry group of $\hat{H} = \hat{H}_0 + \hat{V}$. The reason is that in the first order only a basis change is made in $\underline{V}^p$. The representations $\underline{\tilde{V}}^{p_i}$ that are involved then result, as in Sect. 8.2, from the reduction of $\bar{\Gamma}^p$, i.e. with the help of the respective correlation tables.

Example To provide an example, we revisit the scenario of a particle in a cubic box discussed in Sect. 7.2. Specifically, we focus on the first three eigenspaces, which serve as proper representation spaces of an irreducible representation of O_h. We introduce the term $\hat{V} = \alpha \hat{z}^2$ to the system's Hamiltonian, leading to $G_0 = O_h$ and $G = D_4$. As the first eigenspace of $\hat{H}_0$ is non-degenerate, it cannot experience energetic splitting. Consequently, we examine the second and third eigenspaces:

(i) The eigenspace $\underline{V}^{[1,1,2]}$ belongs to the representation T_{1u}. According to the correlation Table 8.2 it is

$$T_{1u} \overset{O_h \to D_{4h}}{\to} A_{2u} \oplus E_u \,.$$

The states introduced in Sect. 7.2 are already bases of the spaces $\underline{V}^{A_{2u}}$ and $\underline{V}^{E_u}$, where

$$\begin{aligned} A_{2u} &: \Psi_{112} \quad (\sim z) \,, \\ E_u &: \{\Psi_{121}, \Psi_{211}\} \quad (\sim \{x, y\}) \,. \end{aligned}$$

(ii) Likewise, the eigenspace $\underline{V}^{[1,2,2]}$ belongs to the representation T_{1g} and the correlation table yields

$$T_{2g} \overset{O_h \to D_{4h}}{\to} B_{2g} \oplus E_g \,,$$

where

$$\begin{aligned} B_{2g} &: \Psi_{221} \quad (\sim x \cdot y) \,, \\ E_g &: \{\Psi_{122}, \Psi_{212}\} \quad (\sim \{x \cdot y, y \cdot z\}) \,. \end{aligned}$$

It is crucial to understand the following fact: The splitting of G into irreducible representation spaces $\underline{\tilde{V}}^{p_i}$, which occurs at zeroth order, remains valid beyond the realm of perturbation theory. If this was not the case, there had to be a point where, as $\hat{V}$ steadily increases, a sudden transition into a fundamentally different

[4] The first order of degenerate perturbation theory with regard to the energy is also referred to as the zeroth order with regard to the eigenstates.

eigenspace took place. Such a scenario is inconceivable in physical systems, even in the absence of a formal mathematical proof of this statement.

8.4 Application: Splitting of Atomic Orbitals in Crystal Fields

Given the orbitals (s, p, d, …) of an atom, the question arises as to what qualitative changes occur when the atom is placed in an environment that is no longer fully rotationally symmetric (e.g. in a solid). To address this, we examine a Hamiltonian of the form

$$\hat{H} = \underbrace{\frac{\hat{\vec{p}}^2}{2m} + V(|\vec{r}|)}_{\text{atom}} + V_{\text{cf}}(\vec{r}) \equiv \hat{H}_0 + V_{\text{cf}}(\vec{r}) \ ,$$

where $V_{\text{cf}}(\vec{r})$ is commonly known as the *crystal field* in solid-state physics. The symmetry group G_0 of H_0 is not finite, which sets it apart from all other groups discussed in this book. However, we can avoid dealing with such infinite (*Lie*) groups in detail by utilizing our understanding of the spectrum of $\hat{H}_0$:

8.4.1 The Atomic Problem

Remainder: Atomic Spectra

We briefly repeat the essential results for the spectrum of $\hat{H}_0$, which are derived in every textbook on quantum mechanics:

It is $[\hat{H}_0, \hat{L}_i] = 0$ for all three components $\hat{L}_i$ of the orbital angular momentum $\hat{\vec{L}}$. One then usually shows that $\hat{\vec{L}}^2$ and $\hat{L}_z$ have common eigenstates $|l, m\rangle$, with ($\hbar = 1$)

$$\begin{aligned} \hat{\vec{L}}^2 |l, m\rangle &= l(l+1)|l, m\rangle \qquad l = 0, 1, 2, \dots \ , \\ \hat{L}_z |l, m\rangle &= m|l, m\rangle \qquad m = -l, -l+1, \dots, l-1, l \ . \end{aligned}$$

Since $[\hat{H}_0, \hat{\vec{L}}^2] = 0$ and $[\hat{H}_0, \hat{L}_z] = 0$, we can find common eigenstates of all three operators,

$$\hat{H}_0 |n, l, m\rangle = E_{n,l} |n, l, m\rangle \ .$$

With the ladder operators $\hat{L}_\pm$,

$$\hat{L}_\pm |n, l, m\rangle \sim |n, l, m \pm 1\rangle \ ,$$

which also commute with $\hat{H}_0$, it follows, e.g.

$$\begin{aligned}\hat{L}_\pm \hat{H}_0 |n,l,m\rangle &= E_{n,l}\hat{L}_\pm |n,l,m\rangle \sim E_{n,l}|n,l,m\pm 1\rangle \\ &= \hat{H}_0\hat{L}_\pm |n,l,m\rangle \sim \hat{H}_0|n,l,m\pm 1\rangle = E_{n,l}|n,l,m\pm 1\rangle\ .\end{aligned}$$

Therefore, all states $|n,l,m\rangle$ $(m=-l,\ldots,l)$ have the same energy and there is an $(2l+1)$-fold degeneracy of the spectrum. In real space the eigenfunctions (in spherical coordinates) have the form

$$\Psi_{n,l,m}(t,\theta,\varphi) = R_{n,l}(r)Y_{l,m}(\theta,\varphi)\ ,$$

with the spherical harmonics

$$Y_{l,m}(\theta,\varphi) \sim P_l^m(\cos(\theta))e^{\mathrm{i}m\varphi}\ ,$$

and the *associated Legendre polynomials* $P_l^m(\cos(\theta))$. The exact form of the functions $P_l^m(\cos(\theta))$ and $R_{n,l}(r)$ is irrelevant for our following considerations. The wave functions for the lowest values of l are

(i) $l=0$, s-orbitals:

$$Y_{0,0} \sim \text{const}\ ,$$

(ii) $l=1$, p-orbitals:

$$Y_{1,\pm 1} \sim \sin(\theta)e^{\pm\mathrm{i}\varphi},\ Y_{1,0} \sim \cos(\theta)\ ,$$

(iii) $l=2$, d-orbitals:

$$Y_{2,\pm 2} \sim \sin^2(\theta)e^{\pm 2\mathrm{i}\varphi},\ Y_{2,\pm 1} \sim \sin(\theta)\cos(\theta)e^{\pm\mathrm{i}\varphi},\ Y_{2,0} \sim (3\cos^2(\theta)-1)\ ,$$

(iv) $l=3$, f-orbitals:

$$\begin{aligned}&Y_{3,\pm 3} \sim \sin(\theta)^3 e^{\pm 3\mathrm{i}\varphi},\ Y_{3,\pm 2} \sim \sin(\theta)^2\cos(\theta)e^{\pm 2\mathrm{i}\varphi},\\ &Y_{3,\pm 1} \sim \sin(\theta)(5\cos(\theta)^2-1)e^{\pm\mathrm{i}\varphi},\ Y_{3,0} \sim (5\cos(\theta)^3-3\cos(\theta))\ .\end{aligned}$$

Group-Theoretical Treatment of the Problem

The symmetry group of $\hat{H}_0$ is $O(3)$, which comprises of operators $\hat{U}_{\tilde{D}}$ with arbitrary orthogonal matrices $\tilde{D}$. Our objective is to find the representation matrices and, more importantly, the characters of this group (in order to use again (5.23)). To avoid

dealing with infinite groups, we will take a pragmatic approach and make use of the results obtained in Sect. 8.4.1.

As $O(3)$ represents the maximum symmetry group of $\hat{H}_0$, the functions $Y_{l,m}(\theta, \varphi)$ $(m = -l, \ldots, l)$ must form a representation space of dimension $(2l + 1)$ for $O(3)$, as stated by our postulate from Sect. 6.3.3. This enables us to determine some representation matrices and the corresponding characters.

(i) Let $\tilde{D}$ be a matrix that describes a rotation around the z-axis with the angle α. Then obviously

$$\hat{U}_{\tilde{D}} \cdot Y_{l,m}(\theta, \varphi) = e^{-\mathrm{i} \cdot m \cdot \alpha} \cdot Y_{l,m}(\theta, \varphi) \; .$$

The representation matrix of $\tilde{D}$ is therefore diagonal and given as

$$\tilde{\Gamma}^l(\alpha) = \begin{pmatrix} e^{-\mathrm{i}l\alpha} & & & 0 \\ & e^{-\mathrm{i}(l-1)\alpha} & & \\ & & \ddots & \\ 0 & & & e^{\mathrm{i}l\alpha} \end{pmatrix} \; .$$

Using the well-known geometric sum formula, we can calculate the character $\chi^l(\alpha)$ as:

$$\chi^l(\alpha) = \sum_{m=-l}^{l} e^{\mathrm{i} \cdot m \cdot \alpha} = \frac{\sin\left[\left(l + \frac{1}{2}\right)\alpha\right]}{\sin\left[\frac{\alpha}{2}\right]} \; . \tag{8.4}$$

It is worth noting that for other axes of rotation, the representation matrices are not diagonal, but the characters remain independent of the axis, as long as the rotation angle α is the same. Since we will only be using these characters in the following, we do not need to consider the representation matrices of other axes of rotation.

(ii) As one shows in all textbooks on quantum mechanics, the spherical harmonics behave under inversion $\tilde{I}$ as

$$\hat{U}_{\tilde{I}} \cdot Y_{l,m}(\theta, \varphi) = (-1)^l Y_{l,m}(\theta, \varphi) \; .$$

which means that

$$\chi^l(I) = (-1)^l l(l + 1) \; .$$

(iii) For a rotational inversion $\tilde{S} \equiv \tilde{I} \cdot \tilde{D}$ one finds analogously

$$\bar{\chi}^l(\alpha) = (-1)^l \frac{\sin\left[\left(l + \frac{1}{2}\right)\alpha\right]}{\sin\left[\frac{\alpha}{2}\right]} \; . \tag{8.5}$$

In particular, in the special case of a reflection on a plane, we find $\bar{\chi}^l(\alpha = \pi) = 1$ (since $\sin[(l + 1/2)\,\pi] = (-1)^l$).

8.4.2 Splitting of Orbital Energies in Crystal Fields

We can use the character tables of our 32 point groups along with the characters of the group $O(3)$ (derived above) to evaluate the qualitative splitting of atomic orbitals using (5.23).[5] As an example, we consider the case of the group $G = O_h$.

By reducing the subduced representation of the first 4 atomic eigenspaces ($l \leq 2$), we obtain:

$$\Gamma^{(s)}_{l=0} = A_g \ , \tag{8.6}$$
$$\Gamma^{(s)}_{l=1} = T_{1u} \ ,$$
$$\Gamma^{(s)}_{l=2} = E_g + T_{2g} \ ,$$
$$\Gamma^{(s)}_{l=2} = A_{2u} + T_{1u} + T_{2u} \ . \tag{8.7}$$

Real linear combinations of functions $Y_{l,m}(\theta, \varphi)$ and $Y_{l,-m}(\theta, \varphi)$ are called *axial* or *tesseral orbitals*,

$$A_{l,m} \equiv \frac{1}{\sqrt{2}}(Y_{l,m} + Y_{l,-m}) \quad (0 \leq m \leq l) \ ,$$
$$A_{l,-m} \equiv \frac{1}{\sqrt{2}\mathrm{i}}(Y_{l,m} - Y_{l,-m}) \quad (0 < m \leq l) \ .$$

In the case of the s, p and d shells, these are also the orbitals that arise in a cubic environment. For these shells, they are therefore also denoted as *cubic orbitals*. Since all other point groups in solids are sub-groups of O_h, they are also a proper starting point to find the suitable orbitals of the other point groups. In the case of the s and p orbitals, there is no splitting and one finds the (probably well-known) real orbitals

$$\alpha_s(r, \theta, \varphi) = R_s(r) Y_{0,0}(\theta, \varphi),$$
$$\beta_x(r, \theta, \varphi) = \frac{1}{\sqrt{2}} R_p(r) \left[Y_{1,1}(\theta, \varphi) + Y_{1,-1}(\theta, \varphi) \right] \sim x \ ,$$
$$\beta_y(r, \theta, \varphi) = \frac{1}{\sqrt{2}\mathrm{i}} R_p(r) \left[Y_{1,1}(\theta, \varphi) - Y_{1,-1}(\theta, \varphi) \right] \sim y \ ,$$
$$\beta_z(r, \theta, \varphi) = R_p(r) Y_{1,0}(\theta, \varphi) \sim z \ .$$

For the 5 d-orbitals we obtain the triple degenerate t_{2g}-orbitals, which can be written, for example, as follows

[5] A critical reader might object that we have proved (5.23) only for finite groups. In physics, however, we can always argue with the fact that our results agree with the experiment.

Table 8.3 Irreducible representations Γ^p and corresponding basis states φ_b for d-orbitals in environments that belong to the crystallographic point groups O_h, O, T_d, T_h, D_{6h}, D_{4h}

G^{point}	Γ^p	$\{\varphi_b\}$
$[O_h, O, T_d, T_h]$	$[E_g, E, E, E_g]$	φ_u, φ_v
	$[T_{2g}, T_2, T_2, T_g]$	$\varphi_\zeta, \varphi_\eta, \varphi_\xi$
D_{6h}	A_{1g}	φ_u
	E_{2g}	φ_v, φ_ζ
	E_{1g}	$\varphi_\eta, \varphi_\xi$
D_{4h}	A_{1g}	φ_u
	B_{1g}	φ_v
	B_{2g}	φ_ζ
	E_g	$\varphi_\eta, \varphi_\xi$

$$\phi_\xi(r,\theta,\varphi) = \frac{1}{\sqrt{2}} R_{t_{2g}}(r)\left[Y_{2,1}(\theta,\varphi) + Y_{2,-1}(\theta,\varphi)\right] \sim x\cdot z\ , \tag{8.8}$$

$$\phi_\eta(r,\theta,\varphi) = \frac{1}{\sqrt{2}\mathrm{i}} R_{t_{2g}}(r)\left[Y_{2,1}(\theta,\varphi) - Y_{2,-1}(\theta,\varphi)\right] \sim y\cdot z\ ,$$

$$\phi_\rho(r,\theta,\varphi) = \frac{1}{\sqrt{2}\mathrm{i}} R_{t_{2g}}(r)\left[Y_{2,2}(\theta,\varphi) - Y_{2,-2}(\theta,\varphi)\right] \sim x\cdot y\ ,$$

and the double degenerate e_g-orbitals

$$\phi_u(r,\theta,\varphi) = R_{e_g}(r) Y_{2,0}(\theta,\varphi) \sim (3z^2 - r^2)\ ,$$

$$\phi_v(r,\theta,\varphi) = \frac{1}{\sqrt{2}} R_{e_g}(r)\left[Y_{2,2}(\theta,\varphi) + Y_{2,-2}(\theta,\varphi)\right] \sim (x^2 - y^2)\ . \tag{8.9}$$

For the 6 point groups that have at least 16 group elements, we show in Table 8.3 to which representations the 5 d-orbitals belong.

In the case of f orbitals, things are more complicated because the axial orbitals

$$\varphi_a(r,\varphi,\theta)) = \frac{1}{\sqrt{2}\mathrm{i}} R_a(r)\left[Y_{3,2}(\varphi,\theta) - Y_{3,-2}(\varphi,\theta)\right] \sim xyz\ ,$$

$$\varphi_{x'}(r,\varphi,\theta)) = \frac{1}{\sqrt{2}\mathrm{i}} R_{x'}\left[Y_{3,1}(\varphi,\theta) - Y_{3,-1}(\varphi,\theta)\right] \sim y(5z^2 - r^2)\ ,$$

$$\varphi_{y'}(r,\varphi,\theta) = \frac{1}{\sqrt{2}} R_{y'}(r)\left[Y_{3,1}(\varphi,\theta) + Y_{3,-1}(\varphi,\theta)\right] \sim x(5z^2 - r^2)\ ,$$

$$\varphi_z(r,\varphi,\theta) = R_z(r) Y_{3,0}(\varphi,\theta) \sim z(5z^2 - 3r^2)\ ,$$

$$\varphi_{\alpha'}(r,\varphi,\theta) = \frac{1}{\sqrt{2}\mathrm{i}} R_{\alpha'}(r)\left[Y_{3,3}(\varphi,\theta) - Y_{3,-3}(\varphi,\theta)\right] \sim y(3x^2 - y^2)\ ,$$

$$\varphi_{\beta'}(r,\varphi,\theta) = \frac{1}{\sqrt{2}} R_{\beta'}(r)\left[\widetilde{Y}_{3,3}(\varphi,\theta) + Y_{3,-3}(\varphi,\theta)\right]\widetilde{} \sim x(x^2 - 3y^2) \ ,$$

$$\varphi_{\gamma}(r,\varphi,\theta) = \frac{1}{\sqrt{2}} R_{\gamma}(r)\left[\widetilde{Y}_{3,2}(\varphi,\theta) + Y_{3,-2}(\varphi,\theta)\right]\widetilde{} \sim z(x^2 - y^2) \ ,$$

obviously do not form basis states of the representations $A_{2\mathrm{u}}$, $T_{1\mathrm{u}}$, $T_{2\mathrm{u}}$, which we have to find in a cubic environment (see (8.7)). Here, the cubic orbitals are more complicated linear combinations of the spherical harmonics and, expressed by the Cartesian coordinates, given as

$$\begin{aligned}
\varphi_a(r,\varphi,\theta) &\sim xyz \ , \\
\varphi_x(r,\varphi,\theta) &\sim x(5x^2 - 3r^2) \ , \\
\varphi_y(r,\varphi,\theta) &\sim y(5y^2 - 3r^2) \ , \\
\varphi_z(r,\varphi,\theta) &\sim z(5z^2 - 3r^2) \ , \\
\varphi_\alpha(r,\varphi,\theta) &\sim x(y^2 - z^2) \ , \\
\varphi_\beta(r,\varphi,\theta) &\sim y(x^2 - z^2) \ , \\
\varphi_\gamma(r,\varphi,\theta) &\sim z(x^2 - y^2) \ .
\end{aligned}$$

Again, for the 6 point groups that have at least 16 group elements, we show in Table 8.4 to which representations the f-orbitals belong.

Table 8.4 Irreducible representations Γ^p and corresponding basis states φ_b, $\varphi_{b'}$ for f-orbitals in environments that belong to the crystallographic point groups O_h, O, T_d, T_h, D_{6h}, D_{4h}

G^{point}	Γ^p	$\{\varphi_b\}$
$[O_h, O, T_d]$	$[A_{2\mathrm{u}}, A_2, A_1]$	φ_a
	$[T_{1\mathrm{u}}, T_1, T_2]$	φ_x , φ_y, φ_z
	$[T_{2\mathrm{u}}, T_2, T_1]$	φ_α, φ_β, φ_γ
T_h	A_{u}	φ_a
	T_{u}	φ_x, φ_y, φ_z
	T_{u}	φ_α, φ_β, φ_γ
D_{6h}	$A_{2\mathrm{u}}$	φ_z
	$B_{1\mathrm{u}}$	$\varphi_{\alpha'}$
	$B_{2\mathrm{u}}$	$\varphi_{\beta'}$
	$E_{1\mathrm{u}}$	$\varphi_{x'}$, $\varphi_{y'}$
	$E_{2\mathrm{u}}$	φ_a, φ_γ
D_{4h}	$A_{2\mathrm{u}}$	φ_z
	$B_{1\mathrm{u}}$	φ_a
	$B_{2\mathrm{u}}$	φ_γ
	E_{u}	$\varphi_{x'}$, $\varphi_{y'}$
	E_{u}	$\varphi_{\alpha'}$, $\varphi_{\beta'}$

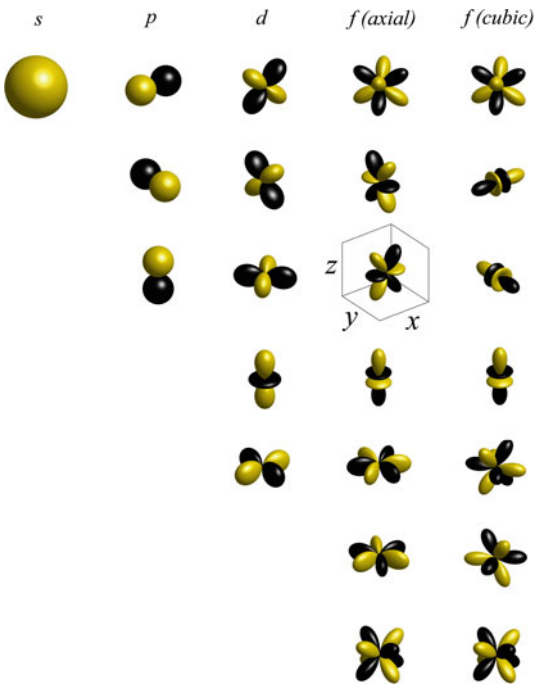

Fig. 8.1 Axial and cubic s, p, d, and f orbitals in the order they have been defined in the main text. For the s, p and d orbitals, the axial and cubic orbitals are identical. This figure was provided to the author by Julian Heckötter, TU Dortmund, Germany

In Fig. 8.1 we show the shape (points with $\Psi(r, \varphi, \theta)^2 = \text{const}$) and the signs (black: $\Psi > 0$, yellow: $\Psi < 0$) of all real orbital wave functions that we have introduced above. The order in the columns of the figure equals that in the corresponding equations of the main text.

8.5 Matrix Elements in Perturbation Theory

Let us revisit the question of which matrix elements of the form ${}_0\langle n|\hat{V}|n'\rangle_0$ disappear and which ones are identical in perturbation theory, assuming that the symmetry group G is a sub-group of G_0. To analyze these, we need to classify the eigenstates of $\hat{H}_0$ group-theoretically in the usual way,

$$|n\rangle_0 \quad \rightarrow \quad |p, m_p, \lambda_p\rangle_0 \ ,$$

such that

$${}_0\langle n|\hat{V}|n'\rangle_0 \quad \rightarrow \quad {}_0\langle p, m_p, \lambda_p|\hat{V}|p', m_{p'}, \lambda_{p'}\rangle_0 \ . \tag{8.10}$$

We assume that $|p, m_p, \lambda_p\rangle_0$ are already the irreducible representation functions for the representation $\bar{\Gamma}^p$ of the symmetry group G of $\hat{H}$, as typically obtained in

degenerate perturbation theory (see Sect. 8.1). For the matrix elements (8.10) it can then be shown, completely analogously to (6.22) and (6.23), that

$$ {}_0\langle p, m_p, \lambda_p | \hat{V} | p', m_{p'}, \lambda_{p'} \rangle_0 = \delta_{p,p'} \delta_{\lambda_p, \lambda_{p'}} V^p_{m_p, m_{p'}} \ , \tag{8.11} $$

where

$$ V^{\tilde{p}}_{m_{\tilde{p}}, m_{\tilde{p}'}} \equiv {}_0\langle \tilde{p}, m_{\tilde{p}}, \lambda_{\tilde{p}} | \hat{V} | \tilde{p}, m_{\tilde{p}'}, \lambda_{\tilde{p}} \rangle_0 \ , $$

is independent of $\lambda_{\tilde{p}}$. With (8.11) we have reached the maximum goal: We now know all matrix elements which are zero and we know the maximum set of matrix elements that have to be determined. There is usually no other systematic way, apart from group theoretical considerations like ours, to reach this goal.

Exercises

1. On a tetrahedral molecule there is an orbital at each of the four vertices. The Hamiltonian of a particle on this molecule is then

$$ \hat{H} = t \sum_{i \neq j = 1}^{4} |i\rangle\langle j| \ . $$

   Determine the eigenstates of this Hamiltonian. To which representation of the group T_d do they belong? Which splittings of the spectrum result, if one of the four edges has a different hopping parameter $t' \neq t$? Interpret this splitting group-theoretically.
2. We consider the system of a particle in a cubic box with infinitely high potential walls as discussed in Sect. 7.2. For the Hamiltonian $\hat{H}_0$ of this system, let us consider a small potential of the form

$$ \hat{V} = f(|\vec{r}|) \cdot \hat{x} \cdot \hat{y} \ . $$

   that is added to $\hat{H}_0$ where $f(|\vec{r}|) > 0$ is an arbitrary function.

   (a) What is the symmetry group of $\hat{H} = \hat{H}_0 + \hat{V}$?
   (b) What are the splittings of the energetic second and third eigenspaces of $\hat{H}_0$ ($\underline{V}^{(2)}$ and $\underline{V}^{(3)}$) are to be expected here for symmetry reasons?
   (c) Which matrix elements $\langle \phi^2_i | \hat{V} | \phi^3_j \rangle$ are non-zero, if $|\phi^2_i\rangle \in \underline{V}^{(2)}$ and $|\phi^3_i\rangle \in \underline{V}^{(3)}$ are the adapted eigenfunctions resulting from the zeroth order of the perturbation theory?

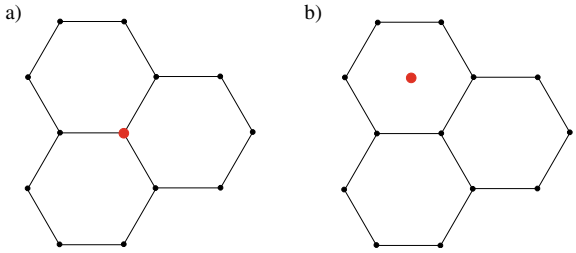

Fig. 8.2 Iron atoms placed on a Honeycomb lattice

Table 8.5 Character table of the group D_{3d}. Here, the mirror plane σ_h is perpendicular to the main rotation axis

D_{3h}	E	$2C_3$	$3C_2'$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_1''	1	1	1	–1	–1	–1
A_2'	1	1	–1	1	1	–1
A_2''	1	1	–1	–1	–1	1
E'	2	–1	0	2	–1	0
E''	2	–1	0	–2	1	0

3. Once again, we look at the particle in the cubic box potential from Sect. 7.2 and add a Dirac delta potential

$$V(\vec{r}) = V_0 \cdot \delta(\vec{r})$$

to it.

   (a) Justify why the system with the potential has the (maximum) symmetry group O_h.
   (b) Show that the third eigenspace (with energy $E = 11\alpha$) in degenerate perturbation theory (first order for the energies) yields exactly the splitting we found in Sect. 7.2.

4. An iron atom is placed on the two-dimensional lattice (honeycomb lattice) shown in Fig. 8.2 either

   (a) on a corner point of one of the hexagons, or
   (b) in the center of a hexagons.

   Which splittings of the five d-orbitals result qualitatively in both cases? In case (a) the point group is D_{3h}, whose characters are given in Table 8.5. The reader will easily find the character table in case (b) online.

5. Consider a particle in a doubly degenerate eigenspace of the group C_{4v}, where the four-fold rotation axis is pointing in the z direction. The corresponding line

Table 8.6 The line from the character table of the group C_{4v} that corresponds to the two-dimensional representation E

C_{4v}		E	$2\delta_4$	$\delta_2 = \delta_4^2$	$2\rho_v$	$2\rho_d$
(x, y)	E	2	0	-2	0	0

from the character table is presented in Table 8.6, where ρ_v represents the mirror planes parallel to the x or y axis.
Suppose we apply an electric field in either the x or z direction. What will be the new symmetry group in each case? Will the doubly degenerate level split up? If so, which representations do the new eigenstates belong to?

Reference

1. A. Messiah, *Quantum Mechanics*, Dover, 1999

Chapter 9
Material Tensors and Tensor Operators

This chapter focuses on material tensors and tensor operators, both of which are dependent on a multiplet of spatial Cartesian coordinates. Material tensors (e.g. the magnetic susceptibility) are real numbers, while tensor operators are linear operators in a Hilbert space. Despite this significant difference, the group-theoretical analysis of both quantities is quite similar, which is why we treat them in a common chapter. Section 9.1 introduces the material tensors, while Sect. 9.2 discusses the product representations, which are central in most parts of this chapter. We determine the independent components of material tensors in Sect. 9.3. Afterwards, we introduce tensor operators in Sect. 9.4 and derive their irreducible components. The relevance of tensor operators will become apparent in the subsequent Chap. 10.

9.1 Material Tensors

9.1.1 Physical Motivation

The reaction of solids to external fields is described by material tensors. For example, applying an electric field $\vec{E}$ in leading linear order results in a dipole moment

$$\vec{P} = \tilde{\alpha}^{(2)} \cdot \vec{E} \ ,$$

where the three-dimensional matrix $\tilde{\alpha}^{(2)}$ is denoted as the *polarization tensor of rank 2* (see Fig. 9.1). In general, of course, $\vec{P} = \vec{P}(\vec{E})$ is a non-linear function of $\vec{E}$ and one can do a Taylor expansion

$$P_i = \sum_j \alpha^{(2)}_{i,j} \cdot E_j + \sum_{j,k} \alpha^{(3)}_{i,j,k} \cdot E_j \cdot E_k + \dots \ , \tag{9.1}$$

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https://doi.org/10.1007/978-3-031-55268-7_9

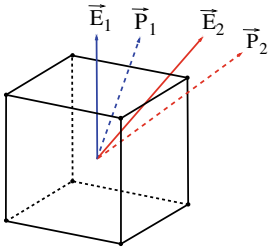

Fig. 9.1 Examples of relationships between an electric field and the dipole moment mediated by the polarization tensor

with *tensors* $\alpha^{(n)}_{i_1,\ldots,i_n}$ *of rank n*. The main goal here is to determine the independent tensor components and their relationships with dependent components. This analysis is relevant both in experimental and theoretical physics as it allows for the determination of the entire tensor by measuring or calculating only the independent components.

9.1.2 Transformation of Tensors

We now consider the contribution of rank n in an expansion of the form (9.1),

$$P^{(n)}_{i_1} = \sum_{i_2,\ldots,i_n} \alpha^{(n)}_{i_1,\ldots,i_n} \cdot E_{i_2} \cdots E_{i_n} \ , \tag{9.2}$$

where $\vec{P}$ and $\vec{E}$ are three-dimensional polar vectors. Here is a quick reminder of the difference between polar and axial vectors: A polar vector such as an electric field and the dipole moment transforms under rotations $\tilde{D}$ as

$$\vec{E}' = \tilde{D} \cdot \vec{E} \quad , \quad \vec{P}' = \tilde{D} \cdot \vec{P} \ . \tag{9.3}$$

In contrast, an axial field (e.g. the magnetic field $\vec{B}$) has the following transformation behavior:

$$\begin{aligned} \vec{B}' &= \tilde{D} \cdot \vec{B} \quad (\text{if } |\tilde{D}| = 1) \ , \\ \vec{B}' &= -\tilde{D} \cdot \vec{B} \quad (\text{if } |\tilde{D}| = -1) \ . \end{aligned}$$

We will first look at the case of polar vectors and the corresponding tensors. At the end of Sect. 9.3 we briefly explain how the entire formalism can also be applied to tensors which describe the connection of axial vectors.

The analysis presented in the following assumes that all quantities in (9.2) are macroscopic and do not depend on the location. In this case, the point group of the solid is relevant in the analysis (as defined in Chap. 3 and more accurately in

Chap. 12). If all variables are spatially dependent, however, the analysis remains the same with the only modification that the point group of the specific location is used.

In a rotated coordinate system, analogously to (9.2), we find

$$P_{l_1}^{(n)'} = \sum_{l_2,\ldots,l_n} \alpha_{l_1,\ldots,l_n}^{(n)'} \cdot E'_{l_2} \cdots E'_{l_n} \,. \tag{9.4}$$

We now want to derive the relationship between $\tilde{\alpha}^{(n)}$ and $\tilde{\alpha}^{(n)'}$. For this we apply (9.3) to (9.4),

$$\sum_{i_1} D_{l_1,i_1} \cdot P_{i_1}^{(n)} = \sum_{\substack{i_2,\ldots,i_n \\ l_2,\ldots,l_n}} \alpha_{l_1,\ldots,l_n}^{(n)'} D_{l_2,i_2} \cdots D_{l_n,i_n} \cdot E_{i_2} \cdots E_{i_n} \,.$$

Both sides are multiplied with D_{l_1,j_1} and the sum over l_1 is carried out. The left hand side then becomes

$$\sum_{i_1,l_1} \underbrace{D_{l_1,j_1}}_{=\left(\tilde{D}^{-1}\right)_{j_1,l_1}} \cdot D_{l_1,i_1} \cdot P_{i_1}^{(n)} = \sum_{i_1} \delta_{i_1,j_1} P_{i_1}^{(n)} = P_{j_1}^{(n)} \,.$$

A comparison with (9.2) yields

$$\alpha_{i_1,\ldots,i_n}^{(n)} = \sum_{l_1,\ldots,l_n} D_{l_1,i_1} \cdots D_{l_n,i_n} \cdot \alpha_{l_1,\ldots,l_n}^{(n)'} \,.$$

Under symmetry transformations of a solid, $\tilde{\alpha}^{(n)}$ should stay the same in all components,[1] i.e. for all g elements $\tilde{D}$ of the symmetry group it must be

$$\alpha_{i_1,\ldots,i_n}^{(n)} = \sum_{l_1,\ldots,l_n} D_{l_1,i_1} \cdots D_{l_n,i_n} \cdot \alpha_{l_1,\ldots,l_n}^{(n)} \,. \tag{9.5}$$

These are g equations that connect the components of $\tilde{\alpha}^{(n)}$. Before we can analyze this relationship in more detail, we need the concept of a *product representation*, already introduced for practice purposes in Exercise 5.2.3 of Chap. 5.

9.2 Product Representations

Let $\bar{\Gamma}^p$, $\Gamma^{p'}$ be irreducible representations of a group G. Then the product representation is defined as

$$\Gamma^{p\otimes p'}_{(ik),(jl)}(a) \equiv \Gamma^{p}_{i,j}(a) \cdot \Gamma^{p'}_{k,l}(a) \tag{9.6}$$

[1] Cartesian coordinate systems which result from each other by symmetry transformations, must lead to identical tensors.

for all $a \in G$. The proof of $\bar{\Gamma}^{p\otimes p'}$ being a representation is simple,

$$\begin{aligned}\Gamma^{p\otimes p'}_{(ik),(jl)}(a\cdot b) &\overset{(9.6)}{=} \Gamma^{p}_{i,j}(a\cdot b)\cdot\Gamma^{p'}_{k,l}(a\cdot b)\\ &= \sum_{n,m}\Gamma^{p}_{i,n}(a)\cdot\Gamma^{p}_{n,j}(b)\cdot\Gamma^{p'}_{k,m}(a)\cdot\Gamma^{p'}_{m,l}(b)\\ &\overset{(9.6)}{=} \sum_{n,m}\Gamma^{p\otimes p'}_{(ik),(nm)}(a)\cdot\Gamma^{p\otimes p'}_{(nm),(jl)}(b)\ ,\end{aligned}$$

where, in the second step, we have used that $\bar{\Gamma}^{p}$, $\bar{\Gamma}^{p'}$ are representations.

Product representations can, of course, also be created with reducible representations. We then denote these as $\bar{\Gamma}\otimes\bar{\Gamma}'$. In this chapter, we will mainly consider such product representations.

Even for two irreducible representations, $\bar{\Gamma}^{p\otimes p'}$ is, in general, reducible. This already follows from the dimension, because if, for example, $\bar{\Gamma}^{p}$ has the maximum occurring dimension d_p of a group, then $\bar{\Gamma}^{p\otimes p}$ has the dimension d_p^2, so it must be reducible. Therefore, in general,

$$\bar{\Gamma}^{p\otimes p'} = \sum_{\tilde{p}} c(p,\,p'|\tilde{p})\cdot\bar{\Gamma}^{\tilde{p}}\ ,$$

with coefficients $c(p,\,p'|\tilde{p})\in\mathbb{N}_0$.

The determination of the coefficients $c(p,\,p'|\tilde{p})$ succeeds as usual with (5.23). For this we need the characters of the product representation, which can readily be calculated,

$$\chi^{p\otimes p'}(a) = \sum_{k,l}\Gamma^{p\otimes p}_{(kl),(kl)}(a) \overset{(9.6)}{=} \sum_{k,l}\Gamma^{p}_{k,k}(a)\cdot\Gamma^{p'}_{l,l}(a) = \chi^{p}(a)\cdot\chi^{p'}(a)\ . \tag{9.7}$$

With (5.23) we then find

$$c(p,\,p'|\tilde{p}) = \frac{1}{g}\sum_{i} r_i\cdot\chi^{p\otimes p'}_i\cdot\left(\chi^{\tilde{p}}_i\right)^* \overset{(9.7)}{=} \frac{1}{g}\sum_{i} r_i\cdot\chi^{p}_i\cdot\chi^{p'}_i\cdot\left(\chi^{\tilde{p}}_i\right)^*\ . \tag{9.8}$$

With this equation and with the help of the character tables, we are now in the position to find all the coefficients of interest.

Example As an example we consider the group D_3, and use its character Table 8.1 to find, for example, for the reduction of $\bar{\Gamma}^{E\otimes E}$:

Table 9.1 The multiplication table for the irreducible representations of the group D_3. Since the table is symmetrical (see (9.8)) we have not specified all elements

D_3	A_1	A_2	E
A_1	A_1	A_2	E
A_2		A_1	E
E			$A_1 + A_2 + E$

$$c(E,E|A_1) = \frac{1}{6}(\underbrace{1}_{=r_1}\cdot\underbrace{2\cdot 2}_{=\chi_1^{E\otimes E}}\cdot\underbrace{1}_{=\chi_1^{A_1}} + 2\cdot(-1)\cdot(-1)\cdot 1 + 3\cdot 0\cdot 0\cdot 1) = 1\ ,$$

$$c(E,E|A_2) = \frac{1}{6}(1\cdot 2\cdot 2\cdot 1 + 2\cdot(-1)\cdot(-1)\cdot 1 + 3\cdot 0\cdot 0\cdot 1) = 1\ ,$$

$$c(E,E|E) = \frac{1}{6}(1\cdot 2\cdot 2\cdot 2 + 2\cdot(-1)\cdot(-1)\cdot(-1) + 3\cdot 0\cdot 0\cdot 0) = 1\ .$$

Hence, we obtain

$$\bar{\Gamma}^{p\otimes p'} = \bar{\Gamma}^{A_1} + \bar{\Gamma}^{A_2} + \bar{\Gamma}^{E}\ .$$

The results of reducing product representations from irreducible representations are summed up in tables known as *multiplication tables*. An example of such a table for the group D_3 can be seen in Table 9.1. It is worth noting that the use of the same names for both these tables and the group multiplication tables is unlikely to cause confusion in most cases. Multiplication tables are readily available on numerous websites.

The multiple product representations are defined in the same way

$$\bar{\Gamma} \equiv \bar{\Gamma}_1 \otimes \bar{\Gamma}_2 \otimes \cdots \otimes \bar{\Gamma}_n\ ,$$

with the representation matrices

$$\Gamma_{I,L}(a) \equiv \Gamma_{(i_1,\ldots,i_n),(l_1,\ldots,l_n)}(a) \equiv \Gamma_{i_1,l_1}(a)\cdot\Gamma_{i_2,l_2}(a)\cdots\Gamma_{i_n,l_n}(a)\ , \tag{9.9}$$

where we have introduced the multiple indices

$$I \equiv (i_1,\ldots,i_n),\ \ L \equiv (l_1,\ldots,l_n)\ . \tag{9.10}$$

9.3 Independent Tensor Components

Our objective now is to identify all the interdependencies among the tensor components α_I and a set of independent components. Although in some specific cases, the components α_I can be selected independently, this is not generally the case. As we

will see shortly, the independent parts of the tensor are typically expressed as linear combinations of the α_I components.

To begin our analysis, using the multiple indices notation (9.10), we first express (9.5) as:

$$\alpha_I = \sum_L \Gamma_{L,I}(a) \cdot \alpha_L \ , \tag{9.11}$$

where[2]

$$\Gamma_{(l_1,\ldots,l_n),(i_1,\ldots,i_n)}(a) \equiv D_{l_1,i_1}(a) \cdots D_{l_n,i_n}(a) \ .$$

Up to this point, we have essentially argued with results from linear algebra. Now we want to bring in our knowledge of group theory. Let

$$\bar{\Gamma} = \sum_p n_p \cdot \bar{\Gamma}^p \ ,$$

be the reduction of $\bar{\Gamma}$ which is generated by some unitary matrix

$$S_{I,(p,m_p,\lambda_p)} \quad (m_p = 1, \ldots, n_p, \lambda_p = 1, \ldots, d_p) \ ,$$

i.e.

$$\tilde{S}^\dagger \cdot \bar{\Gamma} \cdot \tilde{S} = \begin{pmatrix} \bar{\Gamma}^1 & & & & & 0 \\ & \ddots & & & & \\ & & \bar{\Gamma}^1 & & & \\ & & & \ddots & & \\ & & & & \bar{\Gamma}^r & \\ & & & & & \ddots \\ 0 & & & & & \bar{\Gamma}^r \end{pmatrix} . \tag{9.12}$$

With the matrix $\tilde{S}$ we define the new tensor components

$$\beta_{(p,m_p,\lambda_p)} \equiv \sum_I S_{I,(p,m_p,\lambda_p)} \cdot \alpha_I \ ,$$

the inverse of which are given by

$$\alpha_I = \sum_p \sum_{m_p=1}^{n_p} \sum_{\lambda_p=1}^{d_p} S^*_{I,(p,m_p,\lambda_p)} \cdot \beta_{(p,m_p,\lambda_p)} \ . \tag{9.13}$$

[2] Recall that the three-dimensional rotation matrices of a point group are also a (generally reducible) representation (see Exercise 5.2.3 of Chap. 5).

Our objective now is to examine which of the tensor components $\beta_{(p,m_p,\lambda_p)}$ can have non-zero values without violating (9.11). To achieve this, we substitute (9.13) into (9.11),

$$\sum_{p,m_p,\lambda_p} S^*_{I,(p,m_p,\lambda_p)} \beta_{(p,m_p,\lambda_p)} = \sum_{L,p,m_p,\bar{\lambda}_p} \Gamma_{L,I}(a) \cdot S^*_{L,(p,m_p,\bar{\lambda}_p)} \cdot \beta_{(p,m_p,\bar{\lambda}_p)} \ .$$

We multiply this equation with $S_{I,(p',m_{p'},\lambda_{p'})}$ and sum over I. Then, with the unitarity of $\tilde{S}$ and (9.12), it follows

$$\beta_{(p,m_p,\lambda_p)} = \sum_{\bar{\lambda}_p} \Gamma^p_{\lambda_p,\lambda_{p'}}(a) \cdot \beta_{(p,m_p,\bar{\lambda}_p)} \ . \tag{9.14}$$

If we represent the components in a vector with respect to λ_p and $\bar{\lambda}_p$, i.e.

$$\vec{\beta}_{p,m_p} \equiv (\beta_{p,m_p,1}, \ldots, \beta_{p,m_p,d_p})^T \ ,$$

we see that (9.14) simply means that $\vec{\beta}_{p,m_p}$ is an eigenvector of every matrix $\tilde{\Gamma}^p(a)$ to the eigenvalue 1. We will now show that this implies that $\vec{\beta}_{p,m_p} = 0$ for all $p \neq 1$, where $p = 1$ corresponds to the trivial representation A_1, i.e. the one-dimensional representation for which $\Gamma^1(a) = 1$ for all a.

Proof

(i) If $d_p > 1$, the direction of $\vec{\beta}_{p,m_p} \neq \vec{0}$ would be a one-dimensional subspace that is invariant with respect to all $\tilde{\Gamma}^p(a)$. This leads to a contradiction with the statement that we formulated and proved at the beginning of Sect. 4.1.2.

(ii) If $d_p = 1$ and $\beta_{p,m_p} \neq 0$ then it follows

$$\Gamma^p(a) \cdot \beta_{p,m_p} = \beta_{p,m_p} \quad \forall a \ .$$

which proves the statement.

With these findings we can now summarize the main results:

(i) There are exactly n_1 independent tensor components β_{1,m_1}, i.e. as many as the number of occurrences of the representation $\bar{\Gamma}^1$ in the product representation (9.9).

(ii) The tensor α_I can then be written as

$$\alpha_I = \sum_{m_1=1}^{n_1} S^*_{I,(1,m_1)} \cdot \beta_{(1,m_1)} \ . \tag{9.15}$$

where $\beta_{(1,m_1)}$ are the independent tensor components.

As usual, finding the number n_1 is easy in practice because one can use the standard Equation (5.23) for this purpose. The determination of the coefficients $S^*_{I,(1,m_1)}$ in (9.15) is a bit more difficult, but at least possible with elementary methods of linear algebra. The reason is that in (9.12) we are only interested in the sector of the one representation, so we have to consider

$$\tilde{\mathcal{S}}^\dagger \cdot \tilde{\Gamma}(a) \cdot \tilde{\mathcal{S}} = \tilde{1}_{n_1 \times n_1} \ ,$$

instead of (9.12). Here

$$\tilde{\mathcal{S}} = (\vec{s}_1, \ldots, \vec{s}_{n_1}) \ , \tag{9.16}$$

is a rectangular matrix and the vectors $\vec{s}_{m_1}$ are exactly the coefficients $S^*_{I,(1,m_1)}$ in (9.15). When we multiply (9.16) with $\tilde{\mathcal{S}}$ from the left we obtain

$$\tilde{\Gamma}(a) \cdot \tilde{\mathcal{S}} = \tilde{\mathcal{S}} \ .$$

This implies that the vectors $\vec{s}_{m_1}$ are eigenvectors of all matrices $\tilde{\Gamma}(a)$ with an eigenvalue of 1. Although we cannot rule out the possibility that numerical mathematics may offer a better method, we provide a way to solve this problem numerically: First, we determine all eigenvectors of the matrices $\tilde{\Gamma}(a)$ that have an eigenvalue that is not equal to 1. Then, using the singular value decomposition,[3] we can find a basis $\vec{b}_i$ of the subspace spanned by these vectors. The vectors $\vec{s}_{m_1}$ that we need to find must be orthogonal to all $\vec{b}_i$. This leads to a homogeneous linear system of equations given by

$$(\vec{b}_1, \vec{b}_2, \ldots) \cdot \vec{s}_{m_1} = \vec{0} \ .$$

Once more, when it comes to numerically solving this problem, the singular value decomposition is likely the most effective tool.

Example As an example, we consider a polarizability tensor $\tilde{\alpha}^{(2)}$ of rank 2 which we can analyze analytically. This leads to the 9-dimensional representation matrices

$$\Gamma_{(i,j),(k,l)}(a) = D_{i,k}(a) \cdot D_{j,l}(a) \ . \tag{9.17}$$

With these, we obtain for the characters

$$\chi(a) = \underbrace{\sum_i D_{i,i}(a)}_{\equiv \bar{\chi}(a)} \cdot \sum_j D_{i,i}(a) = \bar{\chi}(a)^2 = \bar{\chi}_i^2$$

for all elements in a class $\mathcal{C}_i$. The number n_1 then becomes

[3] William H. Press et al. Numerical Recipes in C: the Art of Scientific Computing. Cambridge [Cambridgeshire]; New York: Cambridge University Press, 1992.

$$n_1 = \frac{1}{g}\sum_i r_i \underbrace{(\chi_i^1)^*}_{=1} \cdot \bar{\chi}_i^2 = \frac{1}{g}\sum_i r_i \cdot \bar{\chi}_i^2 \ . \tag{9.18}$$

The characters $\bar{\chi}(a)$ or $\bar{\chi}_i$ can be calculated with the equation

$$\sum_i D_{i,i}(a) = \pm(2\cos\alpha + 1) \ ,$$

from Sect. 3.3 where α is the rotation angle and the $\pm$ apply to proper and improper rotations.

To provide an illustration, we examine the point groups C_2, C_i, and O_h. Despite the fact that the two groups C_2 and C_i are isomorphic, the outcomes will differ in this particular context because they are not equivalent. Consequently, this serves as a primary example that highlights the insufficiency of classifying groups based solely on isomorphism in physics.

(i) For the group C_2 we have the two matrices

$$\tilde{D}(E) = \tilde{1} \ , \quad \tilde{D}(\delta_2) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \ ,$$

which leads to

$$\bar{\chi}(E) = 3 \ , \quad \bar{\chi}(\delta_2) = -1 \ .$$

By using (9.18), we can determine that there are

$$n_1 = \frac{1}{2}(3^2 + 1) = 5 \ ,$$

independent elements in $\tilde{\alpha}^{(2)}$. To establish the relationship between these components and those from $\tilde{\alpha}^{(2)}$, we need to construct the matrices of the product representation (9.17) and identify their common eigenvectors with eigenvalue 1. In this case, this is easily achievable because

$$\Gamma_{(i,j),k,l}(a) = D_{i,k}(a) \cdot D_{j,l}(a) = \delta_{i,k}\delta_{j,l} D_{i,i} \cdot D_{l,l} \ ,$$

is automatically diagonal. With the arrangement

$$\begin{aligned}(i,j) = (1,1) = 1 \ , (2,2) = 2 \ , \ (3,3) = 3 \ , \ (1,2) = 4 \ , \ (2,1) = 5 \ , \\ (1,3) = 6 \ , \ (3,1) = 7 \ , \ (2,3) = 8 \ , \ (3,2) = 9 \ ,\end{aligned}$$

of the indices we find the product representation matrices

$$\tilde{\Gamma}(E) = \tilde{1} \ , \quad \tilde{\Gamma}(\delta_2) = \begin{pmatrix} 1&0&0&0&0&0&0&0&0 \\ 0&1&0&0&0&0&0&0&0 \\ 0&0&1&0&0&0&0&0&0 \\ 0&0&0&1&0&0&0&0&0 \\ 0&0&0&0&1&0&0&0&0 \\ 0&0&0&0&0&-1&0&0&0 \\ 0&0&0&0&0&0&-1&0&0 \\ 0&0&0&0&0&0&0&-1&0 \\ 0&0&0&0&0&0&0&0&-1 \end{pmatrix} .$$

In this case, the independent components are not linear combinations of the α_I, but the first 5 α_I are themselves such. Therefore we identify,

$$\alpha_{1,1} = \beta_{(p=1,1)} \ , \ \alpha_{2,2} = \beta_{(p=1,2)} \ , \ldots , \alpha_{2,1} = \beta_{(p=1,5)} \ ,$$

whereas

$$\alpha_{1,3} = \beta_{(p=2,1)} = 0 \ , \ \alpha_{3,1} = \beta_{(p=2,2)} = 0 \ , \ \alpha_{2,3} = \beta_{(p=2,3)} = 0 \ , \ \alpha_{3,2} = \beta_{(p=2,4)} = 0 \ .$$

The polarizability tensor $\tilde{\alpha}^{(2)}$, therefore, has the general form

$$\tilde{\alpha}^{(2)} = \begin{pmatrix} \alpha_{1,1} & \alpha_{1,2} & 0 \\ \alpha_{2,1} & \alpha_{2,2} & 0 \\ 0 & 0 & \alpha_{3,3} \end{pmatrix} . \tag{9.19}$$

At first glance it seems strange that $\alpha_{1,2} \neq \alpha_{2,1}$. To clarify this we consider, for example, a body as in Fig. 3.2, i.e. an area in the x-y plane with C_2 symmetry, over which there is a pyramid in z-direction. If we apply an electric field in x or in y direction ($|\vec{E}_x| = |\vec{E}_y|$) to a solid with such a symmetry, it is obvious that the dipole moments

$$P_y = (\tilde{\alpha}^{(2)} \vec{E}_x)_y = \alpha_{1,2} |\vec{E}_x| \ , \quad P_x = (\tilde{\alpha}^{(2)} \vec{E}_y)_x = \alpha_{2,1} |\vec{E}_y| \ ,$$

will not be the same and thus $\alpha_{1,2} \neq \alpha_{2,1}$.

(ii) Let us now consider the group C_i which contains the two elements

$$\tilde{D}(E) = \tilde{1} \ , \quad \tilde{D}(I) = -\tilde{1} \ ,$$

and thus

$$\bar{\chi}(E) = 3 \ , \quad \bar{\chi}(I) = -3 \ .$$

This gives us

$$n_1 = \frac{1}{2}(3^2 + (-3)^2) = 9 \ ,$$

for the number of independent tensor components, i.e. there are no dependencies in the tensor $\tilde{\alpha}^{(2)}$ for this group and none of the matrix elements vanishes.

(iii) In Exercise 4, it is shown that for the group O_h one finds $n_1 = 1$. Thus,

$$\tilde{\alpha}^{(2)} = \alpha \cdot \tilde{1} \ ,$$

i.e. in a cubic solid the polarizability tensor is of the same form as in homogeneous matter like liquids or gases.

In closing this section, we briefly examine tensors containing axial components, such as the magnetic susceptibility tensor $\tilde{\chi}^{(2)}$, which describes the leading order relationship between a magnetic moment and an applied magnetic field, both of which are axial vectors, via the equation

$$\vec{M} = \tilde{\chi}^{(2)} \cdot \vec{B} \ .$$

Here, one can proceed in exactly the same way as in our previous considerations, since the matrices $\tilde{D}'(a)$, defined as (the meaning of G_0 and L_0 is explained in Sect. 3.4)

$$\begin{aligned} \tilde{D}'(a) &\equiv \tilde{D}(a) \ \text{ for } \ |\tilde{D}(a)| = 1 \ (\text{i.e. } a \in G_0) \ , \\ \tilde{D}'(a) &\equiv -\tilde{D}(a) \ \text{ for } \ |\tilde{D}(a)| = -1 \ (\text{i.e. } a \in L_0) \ , \end{aligned}$$

are also a representation of the point group, because

(i) $a, b \in G_0$: it is obviously $\tilde{D}'(a \cdot b) = \tilde{D}'(a) \cdot \tilde{D}'(b)$ $\surd$

(ii) $a \in G_0, b \in L_0$:

$$\tilde{D}'(\underbrace{a \cdot b}_{\in L_0}) = -\tilde{D}(a \cdot b) = (-\tilde{D}(a)) \cdot \tilde{D}(b) = \tilde{D}'(a) \cdot \tilde{D}'(b) \ \surd$$

(iii) $a, b \in L_0$:

$$\tilde{D}'(\underbrace{a \cdot b}_{\in G_0}) = \tilde{D}(a \cdot b) = (-\tilde{D}(a)) \cdot (-\tilde{D}(b)) = \tilde{D}'(a) \cdot \tilde{D}'(b) \ \surd$$

The same then applies to product representations built with the matrices $\tilde{D}'(a)$ $\surd$.

9.4 Tensor Operators

9.4.1 Definition of Tensor Operators

Let us consider a quantum mechanical system with a symmetry group G whose elements of unitary operators are denoted as $\hat{U}_a$. A set of operators $\hat{T}_{i_1,\ldots,i_n}$ is then referred to as *tensor operators of rank n* if they transform according to the following equation,

$$\hat{U}_a \cdot \hat{T}_{i_1,\ldots,i_n} \cdot \hat{U}_a^\dagger = \sum_{l_1,\ldots,l_n} [\Gamma_{l_1,i_1}(a) \cdots \Gamma_{l_n,i_n}(a)] \cdot \hat{T}_{l_1,\ldots,l_n} \ , \tag{9.20}$$

where $\bar{\Gamma}$ is a (usually reducible) representation of G. As examples of such operators, we can consider those that act on the Hilbert space of square-integrable functions.

(i) *Vector operators* are tensor operators of rank $n = 1$. An example are the three components $\hat{x}_i$ of the position vector operator $\hat{\vec{r}}$. They transform like (see Exercise 1)

$$\hat{U}_{\tilde{D}} \cdot \hat{\vec{r}} \cdot \hat{U}_{\tilde{D}}^\dagger = \tilde{D} \cdot \hat{\vec{r}} \ , \tag{9.21}$$

or expressed by the components

$$\hat{U}_{\tilde{D}} \cdot \hat{x}_i \cdot \hat{U}_{\tilde{D}}^\dagger = \sum_j D_{i,j} \cdot \hat{x}_j \ . \tag{9.22}$$

This equation indeed corresponds to (9.20), since $D_{i,j} = (\tilde{D}^{-1})^*_{j,i}$ and the set of matrices $(\tilde{D}^{-1})^*$ is also a representation of a point group. Obviously, the momentum operator $\hat{\vec{p}}$ of a particle is also a vector operator.

(ii) The operators

$$\hat{T}_{i,j} \equiv \hat{x}_i \cdot \hat{x}_j \ ,$$

built with the components of the position vector operator form a tensor operator of rank 2. This is shown in Exercise 6.

(iii) One can also consider the case $n = 0$ (*scalar operators*) which transform like

$$\hat{U}_{\tilde{D}} \cdot \hat{T}_0 \cdot \hat{U}_{\tilde{D}}^\dagger = \hat{T}_0 (= \underbrace{1}_{\tilde{\Gamma}(\tilde{D})=1 \ \forall \tilde{D}} \hat{T}_0) \ ,$$

for all orthogonal matrices $\tilde{D}$, i.e. for all elements of any point group. An example is

$$\hat{\vec{r}}^{\,2} = \hat{x}_1^2 + \hat{x}_2^2 + \hat{x}_3^2 \ ,$$

because

$$\hat{U}_{\tilde{D}} \cdot (\hat{\vec{r}} \cdot \hat{\vec{r}}\,) \cdot \hat{U}_{\tilde{D}}^{\dagger} = \hat{U}_{\tilde{D}} \cdot \hat{\vec{r}} \cdot \underbrace{\hat{U}_{\tilde{D}}^{\dagger} \cdot \hat{U}_{\tilde{D}}}_{=1} \cdot \hat{\vec{r}} \cdot \hat{U}_{\tilde{D}}^{\dagger} \overset{(9.21)}{=} (\tilde{D} \cdot \vec{r}) \cdot (\tilde{D} \cdot \vec{r}) = \hat{\vec{r}}^{\,2} \quad .$$

9.4.2 *Irreducible Tensor Components*

In order to calculate matrix elements of tensor operators, it is necessary to express their components in terms of operators that transform according to irreducible representations. This will be particularly relevant in the next chapter on the Wigner-Eckart Theorem.

Vector Operators

To start, we focus on vector operators $\hat{T}_i$ for simplicity. The extension to general tensor operators will be straightforward.

It is known, as shown in Exercise 5.2.3 of Chap. 5, that the rotation matrices of a point group form a representation of the group:

$$\tilde{\Gamma}(\tilde{D}) \equiv \tilde{D} \ .$$

In general, we can reduce this representation with a unitary matrix $S_{i,(p,m_p,\lambda_p)}$, i.e.

$$\sum_{i,j} S_{j,(p',m_{p'},\lambda'_{p'})} \cdot \Gamma_{j,i} \cdot S_{i,(p,m_p,\lambda_p)} = \delta_{p,p'} \delta_{m_p,m_{p'}} \Gamma^{p}_{\lambda'_p,\lambda_p} \ . \tag{9.23}$$

With this matrix we define the *irreducible tensor components* as

$$\hat{T}_{p,m_p,\lambda_p} \equiv \sum_i S_{i,(p,m_p,\lambda_p)} \cdot \hat{T}_i \ . \tag{9.24}$$

The inversion of this equation reads

$$\hat{T}_i = \sum_{p,m_p,\lambda_p} S^{*}_{i,(p,m_p,\lambda_p)} \cdot \hat{T}_{p,m_p,\lambda_p} \ . \tag{9.25}$$

The irreducible tensor components transform exactly according to the respective irreducible representation matrices, because

$$\hat{U}_a \cdot \hat{T}_{p,m_p,\lambda_p} \cdot \hat{U}_a^\dagger \overset{(9.24)}{=} \sum_i S_{i,(p,m_p,\lambda_p)} \cdot \hat{U}_a \cdot \hat{T}_i \cdot \hat{U}_a^\dagger \overset{(9.20)}{=} \sum_i S_{i,(p,m_p,\lambda_p)} \sum_j \Gamma_{j,i} \cdot \hat{T}_j$$
$$\overset{(9.25)/(9.23)}{=} \sum_{\lambda_p'} \Gamma^p_{\lambda_p',\lambda_p} \cdot \hat{T}_{p,m_p,\lambda_p'} \,. \tag{9.26}$$

Example As an example, we consider again the vector operator $\hat{\vec{r}}$ and the group $G = C_2$. This group has the two elements

$$C_2 = \left\{ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right\} \,,$$

which, considered as representations, are already reduced in this case, i.e. it is

$$\bar{\Gamma} = \bar{\Gamma}^A + 2\bar{\Gamma}^B \,.$$

In this case the operators $\hat{x}_i$ themselves are already irreducible, namely

$$p = A : \hat{T}_{A,1,1} = \hat{x}_3 \quad \text{(symmetric under } \delta_2\text{-rotations)}$$
$$p = B : \hat{T}_{B,1,1} = \hat{x}_1 \quad \text{(antisymmetric under } \delta_2\text{-rotations)}$$
$$p = B : \hat{T}_{B,2,1} = \hat{x}_2 \quad \text{(antisymmetric under } \delta_2\text{-rotations)}$$

General Tensor Operators

Extending the above analysis to arbitrary tensor operators is straightforward. Consider an operator that satisfies (9.20). We then combine the indices as $I = (i_1, \ldots, i_n)$ and $L = (l_1, \ldots, l_n)$ such that (9.20) can be written as

$$\hat{U}_a \cdot \hat{T}_I \cdot \hat{U}_a^\dagger = \sum_L \left[\bar{\Gamma}(a) \otimes \bar{\Gamma}(a) \cdots \otimes \bar{\Gamma}(a) \right]_{L,I} \hat{T}_L \,.$$

The product representation in this equation can also be reduced by means of a unitary matrix $S_{I,(p,m_p,\lambda_p)}$. With this matrix, we again define the irreducible tensor components

$$\hat{T}_{p,m_p,\lambda_p} \equiv \sum_I S_{I,(p,m_p,\lambda_p)} \cdot \hat{T}_I \,,$$

with the inverse

$$\hat{T}_I = \sum_{p,m_p,\lambda_p} S^*_{I,(p,m_p,\lambda_p)} \cdot \hat{T}_{p,m_p,\lambda_p} \,.$$

To summarize this section, any component of a tensor operator can be written as a linear combination of its irreducible components with respect to the symmetry group of the system. This fact will be particularly useful in the next chapter when we evaluate matrix elements of these operators.

Exercises

1. Let $\hat{U}_{\tilde{D}}$ be the unitary operator describing a rotation $\tilde{D}$ in the Hilbert space of the square-integrable functions, i.e. $\langle \vec{r}|\hat{U}_{\tilde{D}}\psi\rangle = \langle \tilde{D}\cdot\vec{r}|\psi\rangle$. Show that then for the position operator holds
$$\hat{U}_{\tilde{D}}\cdot\hat{\vec{r}}\cdot\hat{U}^{\dagger}_{\tilde{D}} = \tilde{D}\cdot\hat{\vec{r}}\,.$$

2. How many independent components has the polarizability tensor $\tilde{\alpha}$ of rank 2 in solids with the point-group symmetries C_3 and D_3?
3. Find out what form the polarizability tensor $\tilde{\alpha}$ of rank 2 has for crystals with the point group C_s.
4. Show that for the group O_h the rank 2 polarizability tensor $\tilde{\alpha}^{(2)}$ has only one independent element, i.e. $n_1 = 1$. Use the result from Exercise 5 in Chap. 7, that the rotation matrices of the group O_h correspond to the irreducible representation T_{1u}.
5. Find out what form the magnetic susceptibility has for crystals with point groups C_2 and C_i.
6. The solution results directly from (9.22),
$$\hat{U}_{\tilde{D}}\cdot\hat{x}_i\cdot\hat{x}_j\cdot\hat{U}^{\dagger}_{\tilde{D}} = \hat{U}_{\tilde{D}}\cdot\hat{x}_i\cdot\hat{U}^{\dagger}_{\tilde{D}}\cdot\hat{U}_{\tilde{D}}\cdot\hat{x}_j\cdot\hat{U}^{\dagger}_{\tilde{D}} \overset{(9.22)}{=} \sum_{l,m} D_{i,l}\cdot D_{j,m}\cdot\hat{x}_l\cdot\hat{x}_m$$
together with the argument after that equation.

Reference

1. William H. Press et al. Numerical Recipes in C: the Art of Scientific Computing. Cambridge [Cambridgeshire]; New York: Cambridge University Press, 1992.

Chapter 10
Matrix Elements of Tensor Operators: The Wigner-Eckart Theorem

In this chapter, we focus on the Wigner-Eckart theorem, which allows us to calculate matrix elements of irreducible tensor components. In Sect. 10.1, we first recall a common variant of this theorem that is usually covered in quantum mechanics courses. In this context, we also introduce the concept of Clebsch-Gordan coefficients. In Sect. 10.2, we explore the significance of matrix elements in perturbation theory. The coupling coefficients, which are crucial in formulating the Wigner-Eckart theorem, are discussed in Sect. 10.3. Finally, in Sect. 10.4, we formulate and proof the Wigner-Eckart theorem with group-theoretical means.

10.1 Clebsch-Gordan Coefficients and the Wigner-Eckart Theorem for Angular Momenta

10.1.1 Clebsch-Gordan Coefficients

As is usually shown in introductory lectures on quantum mechanics, the Hilbert space of a system of two angular momenta $\hat{\vec{J}}_1$, $\hat{\vec{J}}_2$ can be spanned with the base

$$|j_1, m_1; j_2, m_2\rangle \equiv |j_1, m_1\rangle |j_2, m_2\rangle \tag{10.1}$$

where $|j_i, m_i\rangle$ $(m_i = -l_i, \ldots, l_i)$ is the basis of the Hilbert-space of the angular momentum $\hat{\vec{J}}_i$. The basis states (10.1) have the well-known properties ($\hbar = 1$, $i = 1, 2$)

$$\begin{aligned}
\hat{\vec{J}}_i^2 |j_1, m_1; j_2, m_2\rangle &= j_i(j_i+1)|j_1, m_1; j_2, m_2\rangle \ , \\
\hat{J}_{i,z}|j_1, m_1; j_2, m_2\rangle &= m_i|j_1, m_1; j_2, m_2\rangle \quad (m_i = -j_i, \ldots, j_i).
\end{aligned}$$

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An alternative basis consists of eigenstates of $\hat{\vec{J}}^2$, $\hat{J}_z$ and $\hat{\vec{J}}_i^2$ where

$$\hat{\vec{J}} \equiv \hat{\vec{J}}_1 + \hat{\vec{J}}_2 \ .$$

The eigenvalue equations of $\hat{\vec{J}}^2$ and $\hat{J}_z$ are

$$\begin{aligned}
&\hat{\vec{J}}^2 |j, m; j_1, j_2\rangle = j(j+1)|j, m\rangle \ , \quad j = |j_1 - j_2|, |j_1 - j_2| + 1, \ldots, j_1 + j_2 \ , \\
&\hat{J}_z |j, m; j_1, j_2\rangle = m|j, m; j_1, j_2\rangle \ \ m = -j, \ldots, j \ .
\end{aligned}$$

Apparently, the two bases can be expressed by each other,

$$|j, m; j_1, j_2\rangle = \sum_{m_1, m_2} \left(\begin{matrix} j_1 & j_2 \\ m_1 & m_2 \end{matrix} \middle| \begin{matrix} j \\ m \end{matrix} \right) |j_1, m_1; j_2, m_2\rangle \ ,$$

where the coefficients in this equation are denoted as *Clebsch-Gordan coefficients*. How to calculate these coefficients is shown in most books on quantum mechanics. They play a crucial role in the Wigner-Eckart theorem, which we formulate next.

10.1.2 The Wigner-Eckart Theorem for Angular Momenta

Some readers may have already learned about the Wigner-Eckart theorem for angular momenta in their introductory lecture on quantum mechanics. We will briefly review this theorem before generalizing it for general symmetry groups.

Analogous to (9.26), we define a set of $2j + 1$ operators $\hat{T}_{j,m}$ $(m = -j, \ldots, j)$ that behave like

$$\tilde{U}_{\tilde{D}} \cdot \hat{T}_{j,m} \cdot \tilde{U}_{\tilde{D}}^{\dagger} = \sum_{m'=-j}^{j} R^{j}_{m,m'}(\tilde{D}) \cdot \hat{T}_{j,m'}$$

under rotations $\tilde{D} \in O(3)$ as *irreducible spherical tensor operators of rank k*. Here the rotation matrix $R^{j}_{m,m'}(\tilde{D})$ is given by the matrix elements

$$R^{j}_{m,m'}(\tilde{D}) \equiv \langle j, m|\tilde{U}_{\tilde{D}}^{\dagger}|j, m'\rangle$$

of the rotation operator $\tilde{U}_{\tilde{D}}^{\dagger}$ in the subspace j. For example, a tensor operator of rank $j = 1$ consists of three components which results from an arbitrary vector operator $\hat{\vec{V}}$, if we define

$$\hat{T}_{1,\pm 1} \equiv \mp \frac{1}{\sqrt{2}} (\hat{V}_x \pm \hat{V}_y) \ ,$$
$$\hat{T}_{1,0} \equiv \hat{V}_z \ .$$

The Wigner-Eckart theorem then states that for any matrix element of states $|j_1, m_1\rangle$, $|j_2, m_2\rangle$ it holds

$$\langle j_1, m_1 | \hat{T}_{j,m} | j_2, m_2 \rangle = \left(\begin{matrix} j_1 & j_2 \\ m_1 & m_2 \end{matrix} \middle| \begin{matrix} j \\ m \end{matrix} \right) \Omega(j, j_1, j_2) \ , \tag{10.2}$$

with quantities $\Omega(j, j_1, j_2)$, for which it is crucial that they do not depend on m_1, m_2, m. The dependency on the latter quantum numbers is determined entirely by the Clebsch-Gordan coefficients. The calculation or measurement of the matrix elements (10.2) is therefore reduced to determining the usually much smaller number of quantities $\Omega(j, j_1, j_2)$.

10.2 Matrix Elements in the Time-Dependent Perturbation Theory

As discussed in Chap. 8, the evaluation of matrix elements is important in time-independent perturbation theory. However, the evaluation of matrix elements with tensor operators is even more crucial in time-dependent perturbation theory. In this approximation, one typically deals with a Hamiltonian of the form

$$\hat{H}(t) = \hat{H}_0 + f(t) \cdot \hat{V} \ .$$

Let $|p, m_p, \lambda_p\rangle$ be the eigenstates of $\hat{H}_0$. Then, one is mostly interested in transition probabilities which are proportional to matrix elements,

$$W_{(p,m_p,\lambda_p)\to(p',m_{p'},\lambda_{p'})} \sim \langle p', m_{p'}, \lambda_{p'} | \hat{V} | p, m_p, \lambda_p \rangle \ ,$$

In practice, one often has to work with operators $\hat{V}$, which can be expressed by components of tensor operators, e.g.

$$\hat{V} = \vec{E} \cdot \hat{\vec{r}} \quad \text{or} \quad \hat{V} = \vec{A} \cdot \hat{\vec{p}} \ .$$

This is the case, for example, when time-dependent electric ($\vec{E}$) or magnetic fields (expressed by a vector potential $\vec{A}$) act on a system.

Since tensor operators can always be represented by their irreducible components, as shown in Sect. 9.4, the general question arises: what we can learn from group theory about matrix elements of the form[1]

$$W^{p,p',p''}_{\lambda,\lambda',\lambda''} \equiv \langle p, \lambda | \hat{T}_{p',\lambda'} | p'', \lambda'' \rangle \ . \tag{10.3}$$

10.3 Coupling or Clebsch-Gordan Coefficients

The reduction of a product representation of two irreducible representations $\bar{\Gamma}^p$ and $\bar{\Gamma}^{p'}$

$$\bar{\Gamma}^{p \otimes p'} = \sum_{\tilde{p}} C(p, p' | \tilde{p}) \cdot \bar{\Gamma}^{\tilde{p}} \ ,$$

is mediated by the unitary matrix $\tilde{S}$, i.e.

$$\tilde{S}^\dagger \cdot \bar{\Gamma}^{p \otimes p'} \cdot \tilde{S} = \begin{pmatrix} \bar{\Gamma}^1 & & 0 \\ & \ddots & \\ 0 & & \bar{\Gamma}^r \end{pmatrix} \ . \tag{10.4}$$

The representation $\bar{\Gamma}^{\tilde{p}}$ appears in this matrix exactly $C(p, p' | \tilde{p})$ times (similar to (9.12)). In the context of the Wigner-Eckhart theorem, the elements of $\tilde{S}$ are usually written as

$$S_{((p,\lambda),(p',\lambda_{p'})),(\tilde{p},f_{\tilde{p}},\lambda_{\tilde{p}})} = \left(\begin{array}{cc|cc} p & p' & \tilde{p} & f_{\tilde{p}} \\ \lambda & \lambda' & \tilde{\lambda} & \end{array} \right) \quad (f_{\tilde{p}} = 1, \ldots, C(p, p' | \tilde{p})) \ ,$$

and are called *coupling coefficients* (sometimes also denoted as *Clebsch-Gordan coefficients*). The main difference to the Clebsch-Gordan coefficients introduced in Sect. 10.1 is that here an irreducible representation $\tilde{p}$ can occur several times, if

$$C(p, p' | \tilde{p}) > 1 \ .$$

[1] As we will see, the labels $m_p, m_{p'}, m_{p''}$ for the eigenspaces or the different irreducible tensor components are irrelevant here and are therefore dropped in the following considerations.

10.4 The Wigner-Eckhart Theorem

According to the *Wigner-Eckhart theorem*, the matrix elements of the form (10.3) can be expressed as

$$W^{p,p',p''}_{\lambda,\lambda',\lambda''} = \sum_{f_p} \left(\begin{matrix} p'' & p' \\ \lambda'' & \lambda' \end{matrix} \middle| \begin{matrix} p & f_p \\ \lambda & \end{matrix} \right) \Omega(p, p'; p'', f_p) \,, \tag{10.5}$$

where $\Omega(p, p'; p'', f_p)$ are certain quantities, which we will derive during the proof. The significance of this theorem results from the fact that the dependency on λ, λ', λ'' is entirely in the coupling coefficients and independent of the specific form of the operator $\hat{T}_{p',\lambda'}$ and the eigenstates $|p, \lambda\rangle$, $|p'', \lambda''\rangle$. Consequently, to compute the set of all matrix elements $W^{p,p',p''}_{\lambda,\lambda',\lambda''}$, one needs to determine only the (smaller) number of quantities $\Omega(p, p'; p'', f_p)$ either theoretically or experimentally.

Proof The proof is relatively easy due to our preparatory work on the group theoretical foundations. First, we introduce two operators $\hat{1} = \hat{U}_a^\dagger \cdot \hat{U}_a$ into the matrix element, (10.3), left and right of the operator $\hat{T}_{p',\lambda'}$,

$$W^{p,p',p''}_{\lambda,\lambda',\lambda''} = \langle p, \lambda | \hat{U}_a^\dagger \cdot \hat{U}_a \cdot \hat{T}_{p',\lambda'} \cdot \hat{U}_a^\dagger \cdot \hat{U}_a | p'', \lambda'' \rangle \,.$$

With (6.11) and (9.26) we can evaluate the right hand side of this equation,

$$W^{p,p',p''}_{\lambda,\lambda',\lambda''} = \sum_{\bar{\lambda},\bar{\lambda}',\bar{\lambda}''} \left(\Gamma^{p}_{\bar{\lambda},\lambda}(a) \right)^* \underbrace{\Gamma^{p'}_{\bar{\lambda}',\lambda'}(a) \Gamma^{p''}_{\bar{\lambda}'',\lambda''}(a)}_{(x)} \langle p, \bar{\lambda} | \hat{T}_{p',\bar{\lambda}'} | p'', \bar{\lambda}'' \rangle \,. \tag{10.6}$$

Using (10.4) the term (x) can be written as

$$(x) = \sum_{p_0} \sum_{f_{p_0}} \sum_{\lambda_0,\lambda_0'} \left(\begin{matrix} p'' & p' \\ \lambda'' & \lambda' \end{matrix} \middle| \begin{matrix} p_0 & f_{p_0} \\ \lambda_0 & \end{matrix} \right) \left(\begin{matrix} p'' & p' \\ \bar{\lambda}'' & \bar{\lambda}' \end{matrix} \middle| \begin{matrix} p_0 & f_{p_0} \\ \lambda_0' & \end{matrix} \right)^* \Gamma^{p_0}_{\lambda_0,\lambda_0'}(a) \,. \tag{10.7}$$

Now, we can argue in the same way as in Sect. 6.3.5: Since the left side of (10.6) is independent of a, the same applies to the right side. Therefore, we can perform the operation

$$1 = \frac{1}{g} \sum_a \,,$$

on both sides. The a-dependence only shows up in the two green matrix elements in (10.6) and (10.7). With the help of the orthogonality theorem (5.2) we have then proven the Wigner-Eckart theorem (10.5) if we define

Table 10.1 Excerpt of the multiplication table of irreducible representations of the group O_h

O_h	A_{1g}	E_g	T_{1g}	T_{2g}	T_{1u}
A_{1g}	A_{1g}	E_g	T_{1g}	T_{2g}	T_{1u}
E_g		$A_{1g}+A_{2g}+E_g$	$T_{1g}+T_{2g}$	$T_{1g}+T_{2g}$	$T_{1u}+T_{2u}$
T_{1g}			$A_{1g}+E_g+T_{1g}+T_{2g}$	$A_{2g}+E_g+T_{1g}+T_{2g}$	$A_{1u}+E_u+T_{1u}+T_{2u}$
T_{2g}				$A_{1g}+E_g+T_{1g}+T_{2g}$	$A_{2u}+E_u+T_{1u}+T_{2u}$
T_{1u}					$A_{1g}+E_g+T_{1g}+T_{2g}$

$$\Omega(p, p'; p'', f_p) \equiv \frac{1}{d_p} \sum_{\bar{\lambda},\bar{\lambda}',\bar{\lambda}''} \left(\begin{matrix} p'' & p' \\ \bar{\lambda}'' & \bar{\lambda}' \end{matrix} \middle| \begin{matrix} p & f_p \\ \bar{\lambda} & \end{matrix} \right)^* \langle p, \bar{\lambda} | \hat{T}_{p',\bar{\lambda}'} | p'', \bar{\lambda}'' \rangle \ .$$

Example As an example, we consider again the three operators $(\hat{x}, \hat{y}, \hat{z})$ and the group $G = C_2$. This group has the irreducible representations and representation functions

$$\begin{aligned} p &= A : |p_z\rangle \ , \\ p &= B : |p_x\rangle, |p_y\rangle \ . \end{aligned}$$

The multiplication table yields $A \otimes A = A$, $A \otimes B = B \otimes A = B$, $B \otimes B = A$. Hence, it is $C(p, p'|\tilde{p}) > 0$ only if

(i) all p, p', $\tilde{p} = A$, or
(ii) two of the p, p', $\tilde{p}$ are B, one is A.

Thus the following matrix elements are zero

$$\begin{aligned} &\langle p_z|\hat{x}|p_z\rangle \ , \ \langle p_z|\hat{y}|p_z\rangle \\ &\langle p_z|\hat{z}|p_i\rangle \ , \ \langle p_i|\hat{z}|p_z\rangle \ \ i \in \{x, y\} \ , \\ &\langle p_i|\hat{x}|p_j\rangle \ , \langle p_i|\hat{y}|p_j\rangle \ \ (i, j \in (x, y)) \ . \end{aligned}$$

As we have already seen in the case of material tensors, the group C_i, although isomorphic to C_2, can lead to different physics. This is also true in the case of matrix elements, as we show in Exercise 1.

Exercises

1. Find out which of the 27 matrix elements formed with states $|p_x\rangle, |p_y\rangle, |p_z\rangle$ and operators $\hat{x}, \hat{y}, \hat{z}$ are zero when the point group is C_i or C_s where in the latter case x-y may be the mirror plane.
2. The three-dimensional orthogonal matrices $\tilde{D}(a_i)$ defining a point group $G = \{a_1, \ldots, a_g\}$ are known to be a faithful representation $\bar{\Gamma}$ of G. In the following we consider the case $G = O_h$. In Exercise 5 of Chap. 7, it is shown that for the group O_h this representation is irreducible and T_u.

   (a) Determine the irreducible tensor components of the position vector operator

   $$\hat{\vec{r}} = (\hat{x}_1, \hat{x}_2, \hat{x}_3)^T \ .$$

   For which irreducible representations $p, p' \in \{A_{1\mathrm{g}}, E_\mathrm{g}, T_{1\mathrm{g}}, T_{2\mathrm{g}}, T_{1\mathrm{u}}\}$ are then matrix elements of the form

   $$\langle p, \lambda | \hat{x}_i | p', \lambda' \rangle \ ,$$

   necessarily equal to zero? Table 10.1 should help in this task.

   (b) Show that

   $$\hat{T}_{i,j} \equiv \hat{x}_i \cdot \hat{p}_i \ ,$$

   with components $\hat{p}_i$ of the momentum operator is a tensor operator of rank 2. Determine the irreducible tensor components $\hat{T}_{p,m_p,\lambda}$ of $\hat{T}_{i,j}$. Express the $\hat{T}_{i,j}$ in terms of the irreducible components $\hat{T}_{p,m_p,\lambda}$.
   Hint: Using the quadratic representation functions in the character table of O_h, try to find linear combinations of the $T_{i,j}$, which (according to the multiplication Table 10.1) have the expected transformation behavior.

Chapter 11
Double Groups and Their Representations

So far, we have only considered spinless single-particle systems. However, to study electrons, we need to account for their spin and its impact on the symmetry group. This is the topic of Sect. 11.1, where we discuss the changes of the symmetry group when we include the electronic spin. We then introduce double groups, which replace the point groups in this context, in Sect. 11.2. Section 11.3 explains how to determine the multiplication rules of the double groups, which is essential for identifying the classes of the double groups in Sect. 11.4. Finally, in Sect. 11.5, we discuss the irreducible representations of the double groups.

11.1 Particles with Spin 1/2

Consider an electron with spin $1/2$. The corresponding Hilbert space has basis states given by

$$\Psi_{i,\sigma} = \Psi_i(\vec{r}) \cdot |\sigma\rangle$$

where $\Psi_i(\vec{r})$ is a basis of spatial wave functions and $|\uparrow\rangle$, $|\downarrow\rangle$ are the spinor states that correspond to the eigenstates of the spin operator in the z-direction, given by $\hat{S}_z = \frac{1}{2}\tilde{\sigma}_3$. Here, $\tilde{\sigma}_i$ are the well-known Pauli matrices. As shown in Exercise 2 of Chap. 1, a spinor $|\sigma\rangle$ transforms like

$$\tilde{T}_{\vec{\alpha}}|\sigma\rangle = \exp\left(\mathrm{i}\frac{1}{2}\vec{\alpha}\cdot\hat{\tilde{\sigma}}\right)\cdot|\sigma\rangle$$

under a rotation, if we assume that the rotation operator (considered in that Exercise) is the same as for spatial wave functions. Here, $\vec{\alpha}$ is the rotation vector, i.e. the direction of $\vec{\alpha}$ is the axis of rotation and $|\vec{\alpha}|$ is the angle of the rotation. The vector $\hat{\tilde{\sigma}}$ consists of the three Pauli matrices. The 2×2-matrix $\tilde{T}_{\vec{\alpha}}$ can be evaluated

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via its Taylor expansion. To proceed, we need two well-known properties of the Pauli matrices:

$$\tilde{\sigma}_i^2 = \tilde{1} \ ,$$
$$\tilde{\sigma}_i \cdot \tilde{\sigma}_j = \mathrm{i} \sum_k \epsilon_{ijk} \cdot \tilde{\sigma}_k \ .$$

These properties can be expressed concisely as

$$\tilde{\sigma}_i \cdot \tilde{\sigma}_j = \delta_{i,j} + \mathrm{i} \sum_k \epsilon_{ijk} \cdot \tilde{\sigma}_k \ .$$

With any two vectors $\vec{a}, \vec{b} \in \mathbb{R}^3$ we then find

$$(a_i \cdot \tilde{\sigma}_i) \cdot (b_j \cdot \tilde{\sigma}_i) = \delta_{i,j} a_i \cdot b_i + \mathrm{i} \sum_k \epsilon_{ijk} \cdot a_i \cdot b_j \cdot \tilde{\sigma}_k \ ,$$

which, after a summation over i and j on both sides of the equation, yields

$$(\vec{a} \cdot \hat{\tilde{\sigma}}) \cdot (\vec{b} \cdot \hat{\tilde{\sigma}}) = (\vec{a} \cdot \vec{b}) \cdot \tilde{1} + \mathrm{i} \hat{\tilde{\sigma}} \cdot (\vec{a} \times \vec{b}) \ . \tag{11.1}$$

With this equation we are now able to evaluate the Taylor series of $\tilde{T}_{\vec{\alpha}}$,

$$\tilde{T}_{\vec{\alpha}} = \sum_j \frac{1}{j!} \left(\frac{\mathrm{i}}{2} \right)^2 \left(\vec{\alpha} \cdot \hat{\tilde{\sigma}} \right)^j \ .$$

We evaluate the right parenthesis by putting $\vec{a} = \vec{b} = \vec{\alpha}$ into (11.1),

$$(\vec{\alpha} \cdot \hat{\tilde{\sigma}})^j = \begin{cases} (\vec{\alpha})^j & \text{for even } j \\ (\vec{\alpha})^{j-1} (\vec{\alpha} \cdot \hat{\tilde{\sigma}}) & \text{for odd } j \end{cases} \ .$$

With this result, we can conclude the evaluation of the series,

$$\begin{aligned} \tilde{T}_{\vec{\alpha}} &= \sum_{m=0}^{\infty} \frac{1}{(2m)!} \left(\frac{\mathrm{i}}{2} \right)^{2m} |\vec{\alpha}|^{2m} \cdot \tilde{1} + \frac{\vec{\alpha} \cdot \hat{\tilde{\sigma}}}{|\vec{\alpha}|} \sum_{m=0}^{\infty} \frac{1}{(2m+1)!} \left(\frac{\mathrm{i}}{2} \right)^{2m+1} |\vec{\alpha}|^{2m+1} \\ &= \cos \left(\frac{1}{2} |\vec{\alpha}| \right) \cdot \tilde{1} + \mathrm{i} \sin \left(\frac{1}{2} |\vec{\alpha}| \right) \cdot \frac{\vec{\alpha}}{|\vec{\alpha}|} \cdot \hat{\tilde{\sigma}} \ . \end{aligned} \tag{11.2}$$

For a rotation around the angle 2π it follows, for example,

$$\tilde{T}_{2\vec{\pi}} |\sigma\rangle = -|\sigma\rangle$$

i.e. such a rotation

$$\tilde{T}_{2\vec{\pi}} \equiv E^- \tag{11.3}$$

cannot be the group's identity element anymore when applied to a spinor. The identity element results from a rotation with the angle 4π,

$$\tilde{T}_{4\vec{\pi}} = \tilde{T}^2_{2\vec{\pi}} = E \ .$$

11.2 Definition of Double Groups

To account for spin degrees of freedom, as we have seen above, it is necessary to differentiate between angles $\varphi \in (0, 2\pi)$ and $\varphi \in (2\pi, 4\pi)$ for proper rotations. This effectively doubles the number of elements in a point group in all three cases:

(i) $G = G_0$ is a proper point group. In this case the corresponding double group, denoted as $\bar{G}$, is trivially twice as large as G_0.

(ii) $G = \{G_0, L_0\}$ is improper and does not contain the inversion. Then, it is $L_0 = I \cdot G_0'$, where the proper point group G_0' does not contain elements of G_0, as we have shown in Sect. 3.4.1. Therefore, it also results in a doubling of the group size.

(iii) G is improper and contains the inversion,

$$G = G_0 \times (E, I)$$

Due to the doubling of the number of elements in G_0, $\bar{G}$ is also twice as large as G.

Introducing the new pseudo identity element E^- from (11.3) is the simplest way to set up the double groups as follows. If

$$G = \{E, a_2, \ldots, a_g\}$$

is the point group of a spinless system, we can write the double group of the system with spin,

$$\bar{G} = \{E^+, a_2^+, \ldots, a_g^+, E^-, a_2^-, \ldots, a_g^-\} \equiv G^+ \cup G^- \ , \tag{11.4}$$

where $a_i^+ \equiv a_i$ and $a_i^- \equiv E^- \cdot a_i$.

To avoid a misunderstanding, it is important to be cautious at this point. The notation used in (11.4) may give the wrong impression that G is a sub-group of $\bar{G}$ and that $\bar{G}$ can be expressed as

$$\bar{G} = G \times \{E^+, E^-\} \ .$$

If that were the case, then the irreducible representations of $\bar{G}$ would simply be the product of the representations of G and of C_2 (as shown in Exercise 1 of Chap. 5) since the latter is isomorphic to

$$\epsilon \equiv \{E^+, E^-\} .$$

Unfortunately, the situation is more complex because the algebra of the elements a_i has been altered. For instance, for a two-fold rotation, it is no longer true that $(\delta_2)^2 = E$ but we have rather $(\delta_2)^2 = E^-$. Therefore, the subset $E^+, a_2^+, \ldots, a_g^+$ of $\bar{G}$ is not a sub-group of $\bar{G}$ already for the reason not to be closed.

In fact, the sub-group ϵ consisting of E^+ and E^- is a normal sub-group of $\bar{G}$, and the cosets are given by

$$L_{a^+} = L_{a^-} = \{a^+, a^-\} .$$

The factor group $F \equiv \bar{G}/\epsilon$ is then isomorphic to the point group G, with the bijective mapping

$$L_{a^+} \in F \leftrightarrow a \in G .$$

That this is an isomorphism follows from

$$L_{a^+} \cdot L_{b^+} = L_{a^+ \cdot b^+} = L_{(a \cdot b)^+} .$$

Note that the last identity even holds when $a^+ \cdot b^+ \neq (a \cdot b)^+$, as it is the case, e.g. for two rotations about the same axis with an angle π. For these, we find

$$L_{\delta_2^+ \cdot \delta_2^+} = L_{E^-} = L_{E^+} = L_{(\delta_2 \cdot \delta_2)^+}$$

although of course

$$\delta_2^+ \cdot \delta_2^+ = E^- \neq E^+ = (\delta_2 \cdot \delta_2)^+ .$$

In the definition of the double groups, we made the implicit assumption that the symmetry operations should be applied simultaneously to both position space and spinor space (the mathematical details will be discussed in the next section). This requirement is physically justified by the presence of spin-orbit coupling, which may be expressed as

$$\hat{H}_{\text{so}} = \xi \hat{\tilde{L}} \cdot \hat{\tilde{S}} = \xi (\tilde{D} \cdot \hat{\tilde{L}}) \cdot (\tilde{D} \cdot \hat{\tilde{S}}) .$$

When dealing with atoms with a small atomic number, it is a reasonable assumption that the spin-orbit coupling is zero. In such cases, the system's symmetry group can be expressed as a product group, i.e.

$$G_{\xi=0} = G \times SU(2) ,$$

where G is the point group and $SU(2)$ is the group of two-dimensional unitary matrices $\tilde{T}$ with $|T| = 1$ (which can be parameterized as in (11.2)). The irreducible representation spaces of $G_{\xi=0}$ are the product spaces $|p, m_p, \lambda_p\rangle|\sigma\rangle$, as shown in Exercise 1 of Chap. 5. Here, $|p, m_p, \lambda_p\rangle$ represents the representation spaces of G, and $|\sigma\rangle = |\uparrow\rangle, |\downarrow\rangle$. When solving the eigenvalue problem of single-particle systems, one can then disregard the spin and simply attach a label σ to the found spatial eigenstates at the end.

11.3 The Algebra of the Double Groups

The multiplication rules can be established without any difficulties in simple situations, such as consecutive rotations around a single axis. However, to ascertain the algebra of the double group in more complex cases, it is necessary to employ the explicit form of the group elements

$$P(\tilde{D}_i) \equiv (\tilde{D}_i; \tilde{T}_{\vec{\alpha}_i}) \ , \tag{11.5}$$

where $\tilde{D}_i$ are the elements of the point group but with rotation angle vectors

$$0 \leq |\vec{\alpha}_i| \leq 4\pi \ .$$

For the spatial rotation matrices $\tilde{D}_i$ there is, of course, no difference between rotation angles $0 \to 2\pi$ and $2\pi \to 4\pi$. In the case that $\tilde{D}_i$ is a rotational inversion, only the rotational part enters $\tilde{T}_{\vec{\alpha}_i}$.[1] The group multiplication is obviously given as

$$P(\tilde{D}_i) \cdot P(\tilde{D}_j) = (\tilde{D}_i \cdot \tilde{D}_j; \tilde{T}_{\vec{\alpha}_i} \cdot \tilde{T}_{\vec{\alpha}_j}) \ .$$

The point group's multiplication rules for $\tilde{D}_i \cdot \tilde{D}_j$ are not a concern here, because, whether a product of two group elements is of the form a^+ or a^- hinges on whether the angle of rotation $|\vec{\alpha}|$ in the matrix $\tilde{T}_{\vec{\alpha}_i} \cdot \tilde{T}_{\vec{\alpha}_j}$ is larger or smaller than 2π. As an illustration, let us examine rotations about two axes that are not parallel

$$\vec{\alpha}_1 = \frac{3}{2}\pi \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad , \quad \vec{\alpha}_2 = \frac{4}{3}\pi \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \tag{11.6}$$

which, using (11.2), lead to the matrices

$$\tilde{T}_{\vec{\alpha}_1} = \begin{pmatrix} -\frac{1-\mathrm{i}}{\sqrt{2}} & 0 \\ 0 & -\frac{1+\mathrm{i}}{\sqrt{2}} \end{pmatrix} \quad , \quad \tilde{T}_{\vec{\alpha}_2} = \frac{1}{2} \begin{pmatrix} -1+\mathrm{i} & 1+\mathrm{i} \\ -1+\mathrm{i} & -1-\mathrm{i} \end{pmatrix} \ . \tag{11.7}$$

[1] To show this, we would have to deal with the symmetries of the Dirac equation, which is beyond the scope of this book.

The product of these two matrices is given as

$$\tilde{T}_{\vec{\alpha}_1} \cdot \tilde{T}_{\vec{\alpha}_2} = \frac{1}{\sqrt{2}} \begin{pmatrix} -\mathrm{i} & -1 \\ 1 & \mathrm{i} \end{pmatrix} , \tag{11.8}$$

which corresponds to the rotation vector

$$\vec{\alpha} = 3\pi \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}$$

with a rotation angle $|\vec{\alpha}| = 3\pi$.[2] Another example is given in Exercise 2.

The multiplication rules are simpler for rotations around a common axis.

(i) n-fold rotations δ_n:

$$(\delta_n^+)^m = \begin{cases} (\delta_n^m)^+ & \text{for } m < n \\ E^- \in G^- & \text{for } m = n \\ (\delta_n^{m-n})^- \in G^- & \text{for } n < m < 2n \end{cases}$$

(ii) n-fold rotary-inversion axes $\sigma_n = I \cdot \delta_n$

$$(\sigma_n^+)^m = \begin{cases} (\sigma_n^m)^+ & \text{for } m < n \\ \sigma_n^n = I^- & \text{for } m = n \text{ and odd } n \\ \sigma_n^n = E^- & \text{for } m = n \text{ and even } n \\ (\delta_n^{m-n})^- & \text{for } n < m < 2n \end{cases}$$

In the special case of a mirror plane $\sigma = I \cdot \delta_2$, this means

$$(\sigma^+)^2 = E^- \quad , \quad (\sigma^+)^3 = \sigma^- \quad , \quad (\sigma^+)^4 = E^+ \quad .$$

Example As an example, we consider the double group

$$\bar{C}_2 = \{E^+, \delta_2^+, E^-, \delta_2^-\} .$$

This is obviously a cyclic group with the generating element δ_2^+, and therefore $\bar{C}_2$ must be isomorphic to C_4, whose character table we have already given in Table 7.2. We show it again for the elements of $\bar{C}_2$ in Table 11.1. As we will see in the next section, it is no coincidence that in the first two lines the representation of C_2 reappear twice. These representations, however, cannot occur in single-particle systems because they have $\Gamma(E^-) = 1$ and not $\Gamma(E^-) = -1$, as we would expect it due to the spin. The representations in the first two lines, however, can be realized in

[2] $\tilde{T}_{\vec{\alpha}} = (11.8)$ leads to four equations for the elements of $\vec{\alpha}$, which may be solved, e.g. with WolframAlpha.

Table 11.1 Character table of the double group $\bar{C}_2$ which is identical with that of the group D_2

$\bar{C}_2\ (= D_2)$	E^+	δ_2^+	E^-	δ_2^-
Γ_1	1	1	1	1
Γ_2	1	-1	1	-1
Γ_3	1	i	-1	$-$i
Γ_4	1	$-$i	-1	i

multi-particle systems with an even number of particles. Again, the group C_i, although isomorphic to C_2, differs from the latter, since the double group $\bar{C}_i$ is not isomorphic to $\bar{C}_2$ (see Exercise 3). We will consider the representations of the double groups in more detail in Sect. 11.5. Before that, we first have to clarify which classes can appear in double groups.

11.4 The Classes of the Double Groups

To identify the classes of the double groups, it is necessary to have the explicit form (11.5) of the group elements. It is sufficient to examine only proper rotations (or the rotational part of a rotary inversion), as they determine the matrices $\tilde{T}_{\vec{\alpha}}$, which ultimately establish the classes of $\bar{G}$ (provided that we already know the classes of G). The crucial factors here are the spinor matrices $\tilde{T}(\vec{\alpha})$ and their fundamental property given by

$$\tilde{T}(\vec{\alpha} + \vec{\alpha}_\parallel) = -\tilde{T}(\vec{\alpha}) \ , \tag{11.9}$$

where

$$\vec{\alpha}_\parallel \equiv 2\pi \frac{\vec{\alpha}}{|\vec{\alpha}|} \ ,$$

is the 2π rotation with the same rotation axis as that of $\vec{\alpha}$.

When two elements a and b in G belong to different classes in the point group G, their counterparts $a^{+/-}$ and $b^{+/-}$ in the double group will also belong to different classes. This is because the rotation matrices $\tilde{D}$ in (11.5) prevent them to be conjugate. Therefore, we only need to determine under what circumstances two elements a and b in the same class in G will have counterparts $a^{+/-}$ and $b^{+/-}$ in the same class in $\bar{G}$.

First, we want to answer the question of under which circumstances two elements

$$\vec{\alpha} \in G^+ \ ,$$
$$\vec{\alpha} + \vec{\alpha}_\parallel \in G^-$$

can be in the same class in $\bar{G}$. Obviously, this is only possible if there is an angular vector $\vec{\beta}$ for which

$$\tilde{T}(\vec{\alpha}) = \tilde{T}(\vec{\beta})^{-1} \cdot \tilde{T}(\vec{\alpha} + \vec{\alpha}_{\parallel}) \cdot \tilde{T}(\vec{\beta}) \overset{(11.9)}{=} -\tilde{T}(\vec{\beta})^{-1} \cdot \tilde{T}(\vec{\alpha}) \cdot \tilde{T}(\vec{\beta}) \; . \qquad (11.10)$$

The trace of this equation yields

$$\mathrm{Tr}[\tilde{T}(\vec{\alpha})] = -\mathrm{Tr}[\tilde{T}(\alpha)] \; ,$$

which means that

$$\mathrm{Tr}[\tilde{T}(\alpha)] \overset{(11.2)}{=} 2\cos\left(\frac{|\vec{\alpha}|}{2}\right) = 0 \; .$$

Therefore, it must be $|\vec{\alpha}| = \pi$, i.e. only two-fold symmetry axes elements in G^+ and in G^- can be in the same class. Then the question arises, which other rotations $\vec{\beta}$ have to be in G in order to fulfill (11.10). It turns out that $\vec{\beta}$ must be a two-fold axis perpendicular to $\vec{\alpha}$. For example, with $\vec{\alpha} = \pi\vec{e}_z$ and $\vec{\beta} = \pi\vec{e}_x$ we find the matrices

$$\tilde{T}(\vec{\alpha}) = \begin{pmatrix} \mathrm{i} & 0 \\ 0 & -\mathrm{i} \end{pmatrix} \quad , \quad \tilde{T}(\vec{\alpha}'_{\parallel}) = \begin{pmatrix} -\mathrm{i} & 0 \\ 0 & \mathrm{i} \end{pmatrix} \quad , \quad \tilde{T}(\vec{\beta}) = \begin{pmatrix} 0 & \mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \quad ,$$

which in fact satisfy (11.10). In the case where a class $\mathcal{C}$ in G contains two two-fold axes, and the axis perpendicular to these two is also an element of G, the elements $a^{+/-}$ with $a \in \mathcal{C}$ belong to the same class in $\bar{G}$. Similarly, for mirror planes $\sigma = I \cdot \delta_2$, if σ_1 and σ_2 are perpendicular to each other, belong to the same class $\mathcal{C}$, and their intersection line is a two-fold rotation axis in G, then $\sigma_1^{+/-}$ and $\sigma_2^{+/-}$ are also in the same class in $\bar{G}$. Table 11.2 gives the point groups where this applies, and whose corresponding group $\bar{G}$ therefore has a class number $\bar{r}$ that is less than $2r$.

Table 11.2 Groups for which the double group class number $\bar{r}$ is less than $2r$

G	r	$\bar{r}$
D_2, C_{2v}	4	5
D_{2h}	8	10
D_4, C_{4v}, D_{2d}	5	7
D_{4h}	10	14
D_6, C_{6v}, D_{3h}	6	9
D_{6h}	12	18
T	4	7
T_h	8	14
T_d	5	8
O_h	10	16

If a class $C \in G$ does not consist of two-fold axes of rotation or mirror planes, it is

$$\mathrm{Tr}[\tilde{T}(\vec{\alpha})] \neq \mathrm{Tr}[\tilde{T}(\vec{\alpha} + \vec{\alpha}_{\|})] \; .$$

and the corresponding elements in $\bar{G}$ must be split into two classes C^+ and C^-. However, different from what one would spontaneously assume, the classes $\mathcal{C}^+, \mathcal{C}^-$ do not necessarily consist of elements a^+, a^-. The simplest counterexample is the class $\{\delta_3, \delta_3^2\} \in D_3$ where

$$\begin{aligned} \mathrm{Tr}(\tilde{T}(\delta_3^+)) = 1 \quad , \quad \mathrm{Tr}(\tilde{T}(\delta_3^-)) = -1 \\ \mathrm{Tr}(\tilde{T}((\delta_3^2)^+)) = -1; \quad , \quad \mathrm{Tr}(\tilde{T}((\delta_3^2)^-) = 1) \; . \end{aligned}$$

Therefore $\{\delta_3^+, (\delta_3^2)^-\}$ and $\{\delta_3^-, (\delta_3^2)^+\}$ each form a class in $\bar{D}_3$.

11.5 The Irreducible Representations of the Double Groups

Mathematically speaking, we must address the following general issue: Suppose we have a group G with a normal sub-group (in this case, $\epsilon = \{E^+, E^-\}$) and we know the irreducible representations of this sub-group. Then, there exists a general method for determining the irreducible representations of $\bar{G}$ based on this information. Since this textbook caters primarily to physics students, however, we will not delve into the complete mathematical framework here. Instead, we focus solely on the irreducible presentations of the double groups, which come in two forms: symmetric representations that are easily obtained, and more intricate spinor representations.

11.5.1 Symmetric Representations

The following statement holds: If $\bar{\Gamma}^p$ is an irreducible representation of a point group G, then we can obtain an irreducible representation of the corresponding double group by setting

$$\tilde{\Gamma}^p(a^+) = \tilde{\Gamma}^p(a^-) = \tilde{\Gamma}^p(a) \;\; \forall a \in G \; . \tag{11.11}$$

It is obvious that this is a representation. We can show the irreducibility again with (5.25): With the characters $\chi(a)$ of the matrices $\tilde{\Gamma}(a)$ we find

$$\sum_{c \in \bar{G}} |\chi(c)|^2 = \underbrace{\sum_{a^+ \in G^+} |\chi(a^+)|^2}_{=g} + \underbrace{\sum_{a^- \in G^-} |\chi(a^-)|^2}_{=g} = 2g = \bar{g} \; . \; \surd$$

The representations (11.11) are called *symmetric*. They are obviously not realized in single-particle systems (or in many-particle physics with an odd number of particles), since

$$\Gamma(E^-) = \tilde{1} \ ,$$

i.e. there is no sign change for a rotation by 2π.

11.5.2 Extra Representations

All other irreducible representations of the double groups are called *extra representations* or *spinor representations*. To construct them, it makes sense to start with the product matrices

$$\tilde{\Gamma}^{(\mathrm{ex})}(a^{+/-}) \equiv \tilde{\Gamma}^{p}(a) \otimes \tilde{T}(a^{+/-}) \tag{11.12}$$

of the irreducible representation matrices $\tilde{\Gamma}^{p}(a)$ of the point group G and the rotation matrices (11.2) in spin space. Here $\tilde{T}(a^{+/-})$ means that the rotation angle vector belonging to $a^{+/-}$ is inserted into (11.2).

That (11.12) defines r additional representations is obvious. It then remains to be clarified:

(i) Are these representations reducible?
(ii) After the reduction, one has to find out whether some of the resulting irreducible representations are possibly equivalent. For the groups with $\bar{r} < 2r$ this must be the case, because otherwise one would have found more irreducible representations than classes.

Examples We will illustrate this procedure with two examples and otherwise refer to the website https://www.cryst.ehu.es/ where all irreducible representation matrices are listed.

(i) The point group C_2 has the irreducible representations given in Table 6.1. With these we get the two product representations matrices (two because of the $\pm$ signs)

$$\tilde{\Gamma}^{(\mathrm{ex})}(E^+) = \tilde{1} \ , \quad \tilde{\Gamma}^{(\mathrm{ex})}(E^-) = -\tilde{1} \ ,$$
$$\tilde{\Gamma}^{(\mathrm{ex})}(\delta_2^+) = \pm \begin{pmatrix} \mathrm{i} & 0 \\ 0 & -\mathrm{i} \end{pmatrix} \ , \quad \tilde{\Gamma}^{(\mathrm{ex})}(\delta_2^-) = \pm \begin{pmatrix} -\mathrm{i} & 0 \\ 0 & \mathrm{i} \end{pmatrix} \ .$$

Here, both representations are obviously reducible (and already reduced) and equivalent, and we get exactly the two one-dimensional spinor representations as in Table 11.1.

(ii) The point group $\bar{D}_2$ has $\bar{r} = 5$ classes and, therefore, irreducible representations. Since four symmetric representations are already known from the representations of D_2, only one more spinor representation remains to be found.

Using the four one-dimensional representations of D_2 from Table 11.1, we can construct four two-dimensional spinor representations of $\bar{D}_2$ using the product matrices (11.12). Let us consider the first spinor representation, which corresponds to the trivial representation $\Gamma^p(a) = 1\ \forall a$ of D_2 in (11.12):

$$\tilde{\Gamma}^{(\mathrm{ex})}(E^+) = \tilde{1} = -\tilde{\Gamma}^{(\mathrm{ex})}(E^+) \ \ (\to \chi(E^{\pm}) = \pm 2), \tag{11.13}$$

$$\tilde{\Gamma}^{\mathrm{ex}}(\delta^+_{2,x}) = \begin{pmatrix} 0 & \mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} = -\tilde{\Gamma}^{(\mathrm{ex})}(\delta^-_{2,x}) \ \ (\to \chi(\delta^{\pm}_{2,x}) = 0),$$

$$\tilde{\Gamma}^{(\mathrm{ex})}(\delta^+_{2,y}) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = -\tilde{\Gamma}^{(\mathrm{ex})}(\delta^-_{2,y}) \ \ (\to \chi(\delta^{\pm}_{2,y}) = 0),$$

$$\tilde{\Gamma}^{(\mathrm{ex})}(\delta^+_{2,z}) = \begin{pmatrix} \mathrm{i} & 0 \\ 0 & -\mathrm{i} \end{pmatrix} = -\tilde{\Gamma}^{(\mathrm{ex})}(\delta^-_{2,z}) \ \ (\to \chi(\delta^{\pm}_{2,z}) = 0). \tag{11.14}$$

Already this representation is irreducible, which again follows from (5.25),

$$\sum_i r_i |\chi_i|^2 = |\chi(E^+)|^2 + |\chi(E^-)|^2 = 8 = \bar{g} \ \surd$$

where we have used that the characters of all other group elements are equal to zero.

(iii) As a more complicated example, we show (without proof) the character table of the double group $\bar{O}$ in Table 11.3. The representation functions of the symmetric representations are apparently the same as those of the group O. In the spinor representations, the representation functions are 2 or 4 dimensional spaces to the angular momentum $j = 1/2$ or $j = 3/2$.
There is no standardized convention for labeling irreducible representations of double groups. Table 11.4 presents various notations, where the first column is based on the corresponding point groups, although this notation, in the eyes of the author, is the natural one it is rarely used in the literature.

Table 11.3 Character table of the group $\bar{O}$

$\bar{O}$		E^+	E^-	$8C_3^+$	$8C_3^-$	$\begin{matrix}3C_2^+\\3C_2^-\end{matrix}$	$6C_4^+$	$6C_4^-$	$\begin{matrix}6C_2^+\\6C_2^-\end{matrix}$
$x^2+y^2+z^2=r^2$	Γ_1	1	1	1	1	1	1	1	1
	Γ_2	1	1	1	1	1	−1	−1	−1
$(x^2-y^2, 3z^2-r^2)$	Γ_3	2	2	−1	−1	2	0	0	0
	Γ_4	3	3	0	0	−1	1	1	−1
(x, y, z)	Γ_5	3	3	0	0	−1	−1	−1	1
$\left\vert\frac{1}{2};\sigma\right\rangle\left(\sigma=\pm\frac{1}{2}\right)$	Γ_6	2	−2	1	−1	0	$\sqrt{2}$	$-\sqrt{2}$	0
$\Gamma_6\times\Gamma_2$	Γ_7	2	−2	1	−1	0	$-\sqrt{2}$	$\sqrt{2}$	0
$\left\vert\frac{3}{2};\sigma\right\rangle\left(\sigma=\pm\frac{1}{2},\pm\frac{3}{2}\right)$	Γ_8	4	−4	−1	1	0	0	0	0

Table 11.4 Notations of the irreducible representations of $\bar{O}_h$

Notations				Type	Dimension
A_{1g}	Γ_1^+	Γ_1	Γ_1	Sym	1
A_{2g}	Γ_2^+	Γ_2	Γ_2	Sym	1
E_g	Γ_3^+	Γ_3	Γ_{12}	Sym	2
T_{1g}	Γ_4^+	Γ_4	Γ'_{15}	Sym	3
T_{2g}	Γ_5^+	Γ_5	Γ'_{25}	Sym	3
$\bar{E}_{1g}$	Γ_6^+	Γ_6	Γ_6^+	Extra	2
$\bar{E}_{2g}$	Γ_7^+	Γ_7	Γ_7^+	Extra	2
$\bar{G}_g$	Γ_8^+	Γ_8	Γ_8^+	Extra	4
A_{1u}	Γ_1^-	Γ'_1	Γ'_1	Sym	1
A_{2u}	Γ_2^-	Γ'_2	Γ'_2	Sym	1
E_u	Γ_3^-	Γ'_3	Γ'_{12}	Sym	2
T_{1u}	Γ_4^-	Γ'_4	Γ_{15}	Sym	3
T_{2u}	Γ_5^-	Γ'_5	Γ_{25}	Sym	3
$\bar{E}_{1u}$	Γ_6^-	Γ'_6	Γ_6^-	Extra	2
$\bar{E}_{2u}$	Γ_7^-	Γ'_7	Γ_7^-	Extra	2
$\bar{G}_u$	Γ_8^-	Γ'_8	Γ_8^-	Extra	4

Example As an example of a physical system with the symmetry group $\bar{D}_2$, we consider two t_{2g} orbitals (ξ and ρ, see Sect. 8.4.2) with the energies $\epsilon_i = \pm\epsilon$. In the presence of spin-orbit coupling (with coupling strength ζ) the 4-dimensional Hamiltonian has the form[3]

$$\hat{H} = \begin{pmatrix} \epsilon & 0 & 0 & -\zeta \\ 0 & \epsilon & \zeta & 0 \\ 0 & \zeta & -\epsilon & 0 \\ -\zeta & 0 & 0 & -\epsilon \end{pmatrix} .$$

Here, the order of the basis states is

$$|1\rangle = |\xi, \uparrow\rangle, \ |2\rangle = |\xi, \downarrow\rangle, \ |3\rangle = |\rho, \uparrow\rangle, \ |4\rangle = |\rho, \downarrow\rangle \ .$$

The eigenvalues of $\hat{H}$ are

$$E_{1,2} = -\sqrt{\epsilon^2 + \zeta^2} \ ,$$
$$E_{3,4} = \sqrt{\epsilon^2 + \zeta^2} \ ,$$

i.e. we find two doubly degenerate eigenspaces, as it must be, since $\bar{D}_2$ has only one spinor representation which is two-dimensional. The eigenstates, e.g. are

[3] See, for example, [1].

$$|\psi\rangle_1 = \alpha|\xi,\uparrow\rangle + \beta|\rho,\downarrow\rangle \ ,$$
$$|\psi\rangle_2 = -\alpha|\xi,\downarrow\rangle + \beta|\rho,\uparrow\rangle \ .$$

with coefficients α, β which we not need to specify for our further considerations. To show that it is indeed a representation space of the irreducible representation introduced above, we have to show for all classes that the traces of the matrices $\langle\psi_i|\hat{T}_a|\psi_j\rangle$ have the correct value for all 8 elements $\hat{T}_a$ of the group. As an example, we consider $a = \delta_{2z}^+$. With

$$\hat{T}_{\delta_{2,z}^+}|\xi,\sigma\rangle = \mp\mathrm{i}|\xi,\sigma\rangle \ ,$$
$$\hat{T}_{\delta_{2,z}^+}|\rho,\sigma\rangle = \pm\mathrm{i}|\rho,\sigma\rangle \ ,$$

where $\pm$ refers to $\sigma = \uparrow, \downarrow$, we find

$$\hat{T}_{\delta_{2,z}^+}|\psi\rangle_1 = -\mathrm{i}|\psi\rangle_1 \ ,$$
$$\hat{T}_{\delta_{2,z}^+}|\psi\rangle_2 = \mathrm{i}|\psi\rangle_2 \ .$$

Hence, the trace of the matrix $\langle\psi_i|\hat{T}_{\delta_{2,z}^+}|\psi_j\rangle$ is zero, as it has to be.

Exercises

1. We have considered the spinor representations of the double group $\bar{D}_2$ in Sect. 11.5.2. In the subspace of the two t_{2g} orbitals ξ and η with energies $\epsilon_i = \pm\epsilon$, the Hamiltonian of an electron has the matrix form

$$\hat{H} = \begin{pmatrix} \epsilon & 0 & \mathrm{i}\zeta & 0 \\ 0 & \epsilon & 0 & -\mathrm{i}\zeta \\ -\mathrm{i}\zeta & 0 & -\epsilon & 0 \\ 0 & \mathrm{i}\zeta & 0 & -\epsilon \end{pmatrix} \ .$$

   The order of the basis states here is

$$|1\rangle = |\xi,\uparrow\rangle, \ |2\rangle = |\xi,\downarrow\rangle, \ |3\rangle = |\eta,\uparrow\rangle, \ |4\rangle = |\eta,\downarrow\rangle \ .$$

   Determine the eigenstates of the Hamiltonian and check for one of the degenerate eigenspaces if it is a representation space of the spinor representation determined in Sect. 11.5.2.
2. For the rotation angle vectors (11.6) we have calculated the two spinor matrices $\tilde{T}_{\vec{\alpha}_1}, \tilde{T}_{\vec{\alpha}_2}$. Determine $\vec{\alpha}$ for

$$\tilde{T}_{\vec{\alpha}} = \tilde{T}_{\vec{\alpha}_2} \cdot \tilde{T}_{\vec{\alpha}_1} \ .$$

3. Find the multiplication table of the double group $\bar{C}_i$. To which point group of order $g = 4$ is this group isomorphic?
4. What classes does the group $\bar{D}_{2h}$ have? The 8 classes of the group D_{2h} are

$$D_{2h} = \{E\} \cup \{C_2(z)\} \cup \{C_2(y)\} \cup \{C_2(x)\} \cup \{I\} \cup \{\rho(x, y)\} \cup \{\rho(x, z)\} \cup \{\rho(y, z)\} \; .$$

5. Show that the double point group $\bar{C}_3$ is isomorphic to the (cyclic) point group C_6. Which spinor representations does the group $\bar{C}_3$ then have ?
   Hint: Use the fact that C_6 is a cyclic group.

Reference

1. S. Sugano, Y. Tanabe, and H. Kamimura, *Multiplets of Transition-Metal Ions*, Academic Press, 1970

Chapter 12
Space Groups

This chapter focuses on space groups which result from combining rotational symmetries in solids with the translational symmetry. These are obviously the maximum symmetry groups of crystals. In Sect. 12.1, we provide a definition of space groups and discuss their fundamental properties. The space groups can be categorized into two types, symmorphic and non-symmorphic, which we distinguish in Sect. 12.2. Like the point groups, the space groups have both isomorphism and equivalence as distinguishing features. We elaborate on this in Sect. 12.3.

12.1 Definitions

As with the point groups, we want to define the space groups as sub-groups of a continuous group, here the real affine group.

12.1.1 The Real Affine Group

The *real affine group A* consists of all translations and orthogonal (in the following also denoted as rotational) transformations of spatial vectors $\vec{r}$,

$$\vec{r}\,' = \tilde{D} \cdot \vec{r} + \vec{a} \equiv \{\tilde{D}|\vec{a}\} \cdot \vec{r} \ . \tag{12.1}$$

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J. Bünemann, *Group Theory in Physics*, Undergraduate Lecture Notes in Physics,
https://doi.org/10.1007/978-3-031-55268-7_12

The group axioms are obviously satisfied:

(i) The multiplication results as follows: Let $\{\tilde{D}|\vec{a}\}$, $\{\tilde{D}'|\vec{a}'\}$ be elements of A, then

$$\{\tilde{D}|\vec{a}\}\cdot\{\tilde{D}'|\vec{a}'\}\cdot\vec{r} = \{\tilde{D}|\vec{a}\}(\tilde{D}'\cdot\vec{r}+\vec{a}') = \tilde{D}'\cdot\tilde{D}\cdot\vec{r}+\tilde{D}\cdot\vec{a}'+\vec{a} = \underbrace{\{\tilde{D}\cdot\tilde{D}'|\tilde{D}\cdot\vec{a}'+\vec{a}\}}_{\in A}\cdot\vec{r}\ \surd$$

The multiplication of two group elements is therefore given as

$$\{\tilde{D}|\vec{a}\}\cdot\{\tilde{D}'|\vec{a}'\} = \{\tilde{D}\cdot\tilde{D}'|\tilde{D}\cdot\vec{a}'+\vec{a}\}\ . \tag{12.2}$$

(ii) The identity element is $E = \{\tilde{1}|\vec{0}\}$.

(iii) The inverse element is

$$\{\tilde{D}|\vec{a}\}^{-1} = \{\tilde{D}^{-1}|-\tilde{D}^{-1}\cdot\vec{a}\}$$

as can be readily shown with (12.2).

The definition (12.1) of a linear transformation, in which first a rotation and then a translation is carried out, has become established in the literature. Of course, the reverse order is also conceivable and we look at the resulting multiplication rules and the inverse element in Exercise 1.

12.1.2 Space Groups

The *space group of a crystal* is the sub-group of A, which leaves the crystal invariant. In the following, we first introduce a few more definitions and statements and prove the latter afterwards:

(i) The Abelian sub-group of the pure translations

$$T \equiv \left\{\{\tilde{1}|\vec{B}\}\right\}\ ,$$

of a space group G is called the *translation group of* G. We also denote its elements as the *primitive translations*

$$\vec{B} = \vec{B}(n_1,n_2,n_3) = \sum_{i=1}^{3} n_i\cdot\vec{b}_i\ ,$$

where the Bravais basis $\vec{b}_i$ defines the Bravais-lattice of the crystal. In the following we denote the elements of T both as $\{\tilde{1}|\vec{B}\}$ and as a vector $\vec{B}$, depending on the context in which we need them.

(ii) T is a normal sub-group of G, and every element in a coset of T has the same rotational matrix $\tilde{D}$.

(iii) The set of all rotational matrices in G forms a group, denoted as the *point group* G_0 of G.[1] Note, that it still needs to be proven that this set is indeed a group.

(iv) The elements of G_0 preserve the Bravais lattice defined by T, meaning that if $\vec{B} \in T$, then $\tilde{D} \cdot \vec{B} \in T$ for all $\tilde{D} \in G_0$ (with G_0 as defined under (iii)).

Proofs

(i) That T is a group is obviously true.

(ii)+(iv) Let $\{\tilde{D}|\vec{R}\}$ be an element of G and $\{\tilde{1}|\vec{B}\}$ an element of T. Then, with (12.2), we find that

$$\{\tilde{D}|\vec{R}\}^{-1} \cdot \{\tilde{1}|\vec{B}\} \cdot \{\tilde{D}|\vec{R}\} = \{\tilde{1}|\tilde{D}^{-1} \cdot \vec{B}\}$$

is an element of G as well as of T. From this we can conclude

(a) If $\vec{B} \in T$ so is $\tilde{D}^{-1} \cdot \vec{B}$ which proves the statement (iv).

(b) The elements of a class in T are all $\{\tilde{1}|\vec{B}_i\}$ with $\vec{B}_i = \tilde{D} \cdot \vec{B}_j$ for some $\tilde{D} \in G_0$. Therefore T consists of complete classes of G and, because of the criterion in Sect. 2.3.5, it is a normal sub-group which proves the first statement in (ii).

Let $\{\tilde{D}_1|\vec{R}_1\}$ and $\{\tilde{D}_2|\vec{R}_2\}$ be in the same coset with respect to T. Then, by definition of cosets, there are elements $\{\tilde{D}_a|\vec{R}_a\} \in G$ and $\vec{B}_1, \vec{B}_2 \in T$ such that

$$\{\tilde{D}_i|\vec{R}_i\} = \{\tilde{D}_a|\vec{R}_a\} \cdot \{\tilde{1}|\vec{B}_i\} \overset{(12.2)}{=} \{\tilde{D}_a|\tilde{D}_a \cdot \vec{B}_i + \vec{R}_a\} \,.$$

Therefore it is $\tilde{D}_i = \tilde{D}_a$, i.e. all $\tilde{D}_i$ in a coset have the same rotation matrix, which proves the second statement in (ii).

(iii) To prove that the set G_0 is a group, we must demonstrate that it satisfies the group axioms. Let $\tilde{D}_1$, $\tilde{D}_2$ be an element of G_0. By definition, there exist vectors $\vec{R}_1$ and $\vec{R}_2$ such that $\{\tilde{D}_1|\vec{R}_1\}$, $\{\tilde{D}_2|\vec{R}_2\} \in G$. Therefore, the product

$$\{\tilde{D}_1|\vec{R}_1\} \cdot \{\tilde{D}_2|\vec{R}_2\} = \{\tilde{D}_1 \cdot \tilde{D}_2|\tilde{D}_2 \cdot \vec{R}_2 + \vec{R}_1\}$$

is also an element of G. Thus, $\tilde{D}_1 \cdot \tilde{D}_2 \in G_0$.
Furthermore, from Sect. 12.1.1 (iii) with $\tilde{D} \in G_0$, it follows that $\tilde{D}^{-1} \in G_0$. Therefore, G_0 satisfies the group axioms, and we have shown that G_0 is a group.

The definition of the point group G_0 of a crystal has two generalizations compared to our earlier definition in Chap. 3.

(i) The earlier definition of point groups was based on a specific origin. Our new definition, however, illustrated by the two-dimensional example in Fig. 12.1, no

[1] These groups are not always the same as the ones we introduced in Sect. 3.3, see Sect. 12.2.2.

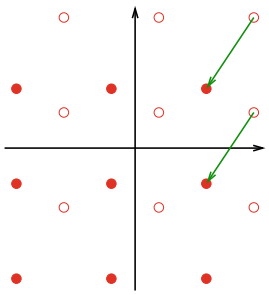

Fig. 12.1 An example for the fact that the point group of a space group is independent of the choice of the origin of the coordinate system, see the main text

longer requires an origin to be specified. The filled dots in the figure indicate a square lattice. The coordinate system is chosen such that the point group is C_1 according to our previous definition in Chap. 3. To obtain the maximum point group of the lattice, one had to place the origin on one of the lattice points.
With our new definition, however, we can perform a rotation of π about an arbitrary point, such as the origin in Fig. 12.1, which transforms the lattice onto the open points. A non-primitive translation, represented by the green vectors, then defines an element of the space group together with the rotation. The rotation of π is therefore an element of G_0, independent of the origin of the coordinate system.
Mathematically, a shift $\vec{R}_0$ of the origin defines an isomorphism between the two space groups G and G',

$$\{\tilde{D}|\vec{R}\} \leftrightarrow \{\tilde{1}|\vec{R}_0\}^{-1} \cdot \{\tilde{D}|\vec{R}\} \cdot \{\tilde{1}|\vec{R}_0\} = \{\tilde{D}|\vec{R} + \tilde{D} \cdot \vec{R}_0 - \vec{R}_0\} \,. \tag{12.3}$$

(ii) Suppose it is $\tilde{D} \in G_0$ (i.e. there is a vector $\vec{R}$ with $\{\tilde{D}|\vec{R}\} \in G$) with $\{\tilde{D}|\vec{0}\} \notin G$ (like in Fig. 12.1). Then the question arises: is there always a shift $\vec{R}_0$ of the origin such that

$$\vec{R} + \tilde{D} \cdot \vec{R}_0 - \vec{R}_0 = \vec{0}$$

and thus

$$\{\tilde{D}|\vec{0}\} \in G' \; \forall \tilde{D} \in G_0 \; ?$$

As we will see in the next section, it is not always possible to find a vector that satisfies this condition. This means that certain crystals have space groups where some elements of G_0 only represent a symmetry transformation when combined with a translation. Such crystals are known as *non-symmorphic crystals*.

12.2 Symmorphic and Non-symmorphic Space Groups

12.2.1 Non-primitive Translations

Below, we will demonstrate that it is possible to express every element of a crystal's space group G in the form of $\{\tilde{D}|\vec{v}_{\tilde{D}} + \vec{B}\}$, where $\vec{B} \in T$ and $\vec{v}_{\tilde{D}}$ is a vector known as the *non-primitive translations*. Using this representation, we can then write[2]

$$G = \sum_{\tilde{D}\in G_0} T \cdot \{\tilde{D}|\vec{v}_{\tilde{D}}\} \equiv \sum_{\vec{B}} \sum_{\tilde{D}\in G_0} \{\tilde{D}|\vec{B} + \vec{v}_{\tilde{D}}\} \,,$$

where $\{\tilde{D}|\vec{v}_{\tilde{D}}\}$ is obviously an element of a coset of T. Each space group is thus uniquely characterized by

(i) T ,
(ii) G_0 ,
(iii) vectors $\vec{v}_{\tilde{D}}$ $(\forall \tilde{D} \in G_0)$.

However, it should not be misconstrued that every combination of T, G_0, and vectors $\vec{v}_{\tilde{D}}$ defines a valid space group. For instance, the condition

$$\vec{B} \in T \quad \Rightarrow \tilde{D} \cdot \vec{B} \in T$$

or all $\tilde{D} \in G_0$ must be satisfied.

Proof If $\{\tilde{D}|\vec{R}\} \in G$ and $\{\tilde{D}|\vec{R}'\} \in G$, then also

$$\{\tilde{D}|\vec{R}\} \cdot \{\tilde{D}|\vec{R}'\}^{-1} = \{\tilde{1}|\vec{R} - \vec{R}'\} \,.$$

Therefore, $\vec{R} - \vec{R}' = B \in T$ and, hence, the vector $\vec{v}_{\tilde{D}}$ is uniquely defined for each $\tilde{D}$.

12.2.2 Difference Between Symmorphic and Non-symmorphic Space Groups

As shown in (12.3), a shift $\vec{R}_0$ of the origin only leads to a shift of the non-primitive translations

$$G = \sum_{\tilde{D}\in G_0} T \cdot \{\tilde{D}|\vec{v}_{\tilde{D}}\} \;\rightarrow G' = \sum_{\tilde{D}\in G_0} T \cdot \{\tilde{D}|\underbrace{\vec{v}_{\tilde{D}} + \tilde{D}\vec{R}_0 - \vec{R}_0}_{\equiv \vec{v}'_{\tilde{D}}}\} \,. \tag{12.4}$$

[2] The summation symbols are to be understood here again in the sense of set unions.

Fig. 12.2 Example of a glide reflection symmetry

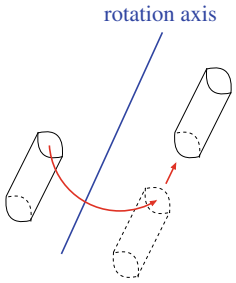

Fig. 12.3 Example of a screw axis symmetry

A space group is denoted as *symmorphic* if there exists a vector $\vec{R}_0$ such that $\vec{v}'_{\tilde{D}} = \tilde{0}$ for all $\tilde{D} \in G_0$ (with $\vec{v}'_{\tilde{D}}$ defined in (12.4)). Conversely, if no such vector exists, the space group is denoted as *non-symmorphic*. The following statement is true:

(i) If G is symmorphic, then G_0 is isomorphic to a sub-group of G since by selecting the origin such that all $\vec{v}_{\tilde{D}} = \tilde{0}$, we find that

$$\{\tilde{D}|\vec{0}\} \in G \quad \forall \tilde{D} \in G_0 \; .$$

In this case, each element of the space group can be written as

$$\{\tilde{D}|\vec{R}\} = \{\tilde{1}|\vec{R}\} \cdot \{\tilde{D}|\vec{0}\} \; .$$

(ii) There exist two categories of symmetry transformations that render a space group non-symmorphic:

(a) Glide reflection: This transformation comprises of reflecting an object across a plane and then translating it. Figure 12.2 illustrates this operation.
(b) Screw axis: This transformation involves rotating an object around an axis while simultaneously translating it. An example is given in Fig. 12.3.

12.3 Inequivalent Space Groups

Already in Chap. 3, we discussed why differentiating point groups only if they are not isomorphic is an insufficient way in physics. Instead, we considered the point groups to be different if they are inequivalent, which led us to identify a total of 32 distinct groups present in solids. We will now use a similar approach to classify space groups.

12.3.1 Matrix Space Groups

For each space group with elements $\{\tilde{D}|\vec{R}\}$ we define a 4-dimensional and real *matrix space group* that is isomorphic to it, via

$$\{\tilde{D}|\vec{R}\} \quad \leftrightarrow \quad \begin{pmatrix} 1 & 0 \\ \vec{R} & \tilde{D} \end{pmatrix} .$$

The isomorphism follows directly:

$$\begin{array}{ccc} \{\tilde{D}|\vec{R}\} \cdot \{\tilde{D}'|\vec{R}'\} & \leftrightarrow & \begin{pmatrix} 1 & 0 \\ \vec{R} & \tilde{D} \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 \\ \vec{R}' & \tilde{D}' \end{pmatrix} \\ \| & & \| \\ \{\tilde{D} \cdot \tilde{D}'|\tilde{D} \cdot \vec{R}' + \vec{R}\} & \leftrightarrow & \begin{pmatrix} 1 & 0 \\ \vec{R} + \tilde{D} \cdot \vec{R}' & \tilde{D} \cdot \tilde{D}' \end{pmatrix} . \end{array}$$

Similar to our prior remarks regarding the 32 point groups observed in solids, we can now express that there are precisely 230 distinct matrix space groups. Among them, 73 are classified as symmorphic.

All translation groups T with elements

$$\{\tilde{1}|\vec{B}\} \hat{=} \begin{pmatrix} 1 & 0 \\ \vec{B} & \tilde{1} \end{pmatrix}$$

are equivalent (and thus isomorphic), because a transformation $\tilde{S}$ between the two sets of Bravais basis vectors, induces a similarity transformation for the corresponding matrix space groups:

$$\begin{pmatrix} 1 & 0 \\ \vec{B} & \tilde{1} \end{pmatrix} \rightarrow \begin{pmatrix} 1 & 0 \\ \vec{0} & \tilde{S} \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 \\ \vec{B} & \tilde{1} \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 \\ \vec{0} & \tilde{S}^{-1} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ \tilde{S} \cdot \vec{B} & \tilde{1} \end{pmatrix} .$$

12.3.2 The 14 Inequivalent Bravais Lattices

In Chap. 3, we had grouped the Bravais lattices into seven crystal systems according to the point groups realized in solids. The classification regarding the space groups leads to the following statement: In Bravais lattices there are exactly 14 inequivalent space groups (or more precisely: matrix space groups) realized. Since these space groups are symmorphic, they are uniquely characterized by specifying the point group G_0 (seven crystal systems) and the translation group T. The resulting 14 Bravais lattices are shown in Fig. 12.4. As discussed in most introductory textbooks on solid-state physics, all 14 cases (including the non-simple lattices) are in fact

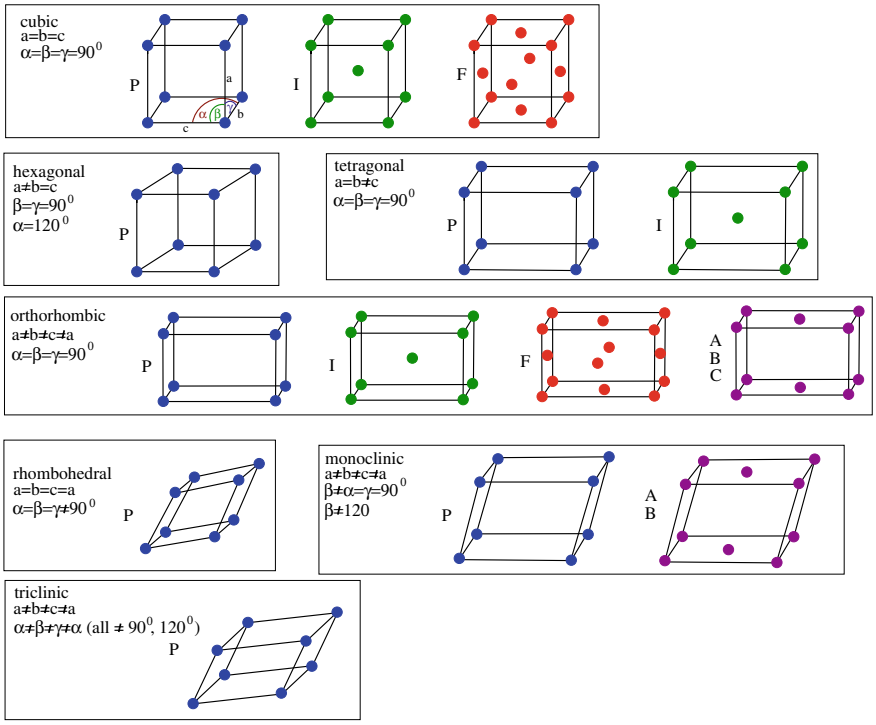

Fig. 12.4 The 14 space groups realized in Bravais lattices (P: simple, B: body-centered, F: face-centered, A/B/C: side-centered)

Bravais lattices. For example, the basis vectors $\vec{b}_i$ in the three cubic cases are (with a lattice constant $a = 1$):

- Simple

$$\begin{aligned} \vec{b}_1 &= (1, 0, 0)^T \\ \vec{b}_2 &= (0, 1, 0)^T \\ \vec{b}_3 &= (0, 0, 1)^T \end{aligned} \tag{12.5}$$

- Body-centered

$$\begin{aligned} \vec{b}_1 &= (-1, 1, 1)^T \\ \vec{b}_2 &= (1, -1, 1)^T \\ \vec{b}_3 &= (1, 1, -1)^T \end{aligned} \tag{12.6}$$

- Face-centered

$$\begin{aligned}\vec{b}_1 &= (0,1,1)^T \\ \vec{b}_2 &= (1,0,1)^T \\ \vec{b}_3 &= (1,1,0)^T\end{aligned} \tag{12.7}$$

12.3.3 Classification of Space Groups

For the classification of a space group, the specification of G_0 and the Bravais lattice (plus the non-trivial translations in non-symmorphic space groups) is sufficient. For crystals, however, the choice of the Bravais lattice (and its crystal class) is in general not unique. For example, the two-dimensional crystal in Fig. 3.10 has a point group $G_0 = C_1$. All space groups with such a point group are equivalent and isomorphic no matter how we choose the vectors $\vec{b}_i$.

As already discussed in Sect. 3.6, it is mathematically possible in this lattice to choose $|\vec{b}_1| = |\vec{b}_2|$ and $\vec{b}_1 \cdot \vec{b}_2 = 0$ i.e. to place the molecules on a perfect square lattice. Physically, however, such a solid cannot exist, since the non-existing symmetry of the molecules would also distort the perfect symmetry of the Bravais lattice.

Table 12.1 The 73 symmorphic space groups. The symbols P, I, F, A, C are explained in Fig. 12.4

Crystal system	Bravais lattice	Space group
Cubic	P	P23, Pm3, P432, P$\bar{4}3m$, P$m3m$
	I	I23, Im3, I432, I$\bar{4}3m$, I$m3m$
	F	F23, Fm3, F432, F$\bar{4}3m$, F$m3m$
Hexagonal	P	P6, P$\bar{6}$, P6/m, P622, P6mm, 2× P$\bar{6}m$2,
		P6/mmm
Tetragonal	P	P4, P$\bar{4}$, P4/m, P422, P4mm, P42m, P$\bar{4}m$2, P4/mmm
	I	I4, I$\bar{4}$, I4/m, I422, I4mm, I42m, I$\bar{4}m$2, I4/mmm
Rhombohedral	R(≙P)	R3, R$\bar{3}$, R32, R3m, R$\bar{3}$3
Orthorhombic	P	P222, Pmm2, Pmmm
	C or A	C222, Cmm2, Amm2, Cmmm
	I	I222, Imm2, Immm
	F	F222, Fmm2, Fmmm
Monoclinic	P	P2, Pm, P2/m
	B	B2, Bm, B2/m
Triclinic	P	P1, P$\bar{1}$

Table 12.2 Abbreviations of some point group symbols in the international notation

Full symbol	Abbreviation
$2mm$	mm
$\frac{2}{m}\frac{2}{m}\frac{2}{m}$	mmm
422	42
$\frac{4}{m}\frac{2}{m}\frac{2}{m}$	$4/mmm$
$\bar{3}\frac{2}{m}$	$\bar{3}m$
622	62
$\frac{6}{m}\frac{2}{m}\frac{2}{m}$	$6/mmm$

Therefore, one chooses that Bravais lattice for the classification of a space group that can be realized physically. For example, in Table 12.1 we list all 73 symmorphic space groups. Note that some space groups have the same symbol and differ only in how the symmetry axes are positioned relative to the base vectors of the Bravais lattice. Some point group symbols here are abbreviated, as listed in Table 12.2.

Exercise

1. Let us assume that affine transformations are defined differently (than in the literature) as follows

$$\vec{r}' = \tilde{D} \cdot (\vec{r} + \vec{a}) \equiv \{\tilde{D}|\vec{a}\} \cdot \vec{r} \ .$$

   What are then the multiplication rules of two group elements and what is the inverse element?

Chapter 13
Representations of Space Groups

In Sect. 13.1, we begin this chapter by discussing the irreducible representations of the translation group as a preparation for Sect. 13.2, where we delve into the irreducible representations of symmorphic space groups.

13.1 Irreducible Representations of the Translation Group

As discussed in Chap. 12, the translation group T is given by the set of all primitive translations

$$\vec{B}(\{n_i\}) = \sum_{i=1}^{3} n_i \cdot \vec{b}_i \ ,$$

where the three vectors $\vec{b}_i$ are again the basis of the Bravais lattice. We now make T and thus the space groups finite by introducing the periodic boundary conditions

$$\{\tilde{D}|\vec{R} + N \cdot \vec{b}_i\} \stackrel{!}{=} \{\tilde{D}|\vec{R}\} \qquad \forall i = 1, 2, 3 \ .$$

Then

$$T = T_1 \times T_2 \times T_3 \ ,$$

where T_i is a cyclic group of order N whose elements are generated by $\vec{b}_i \widehat{=} \{\tilde{1}|\vec{b}_i\}$, i.e. it is

$$\begin{aligned} T_i &= \left\{\{\tilde{1}|\vec{0}\}, \{\tilde{1}|\vec{b}_i\}, \{\tilde{1}|\vec{b}_i\}^2 = \{\tilde{1}|2\vec{b}_i\}, \ldots, \{\tilde{1}|\vec{b}_i\}^{N-1} = \{\tilde{1}|(N-1)\vec{b}_i\}\right\} \\ &\widehat{=} \left\{\vec{0}, \vec{b}_i, 2\vec{b}_i, \ldots, (N-1)\vec{b}_i\right\} \end{aligned}$$

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J. Bünemann, *Group Theory in Physics*, Undergraduate Lecture Notes in Physics,
https://doi.org/10.1007/978-3-031-55268-7_13

where we have used the vectors $\vec{b}_i$ as a shorter expression of the group elements $\{\tilde{1}|\vec{b}_i\}$. The Abelian groups T_i (and thus T) possess N (or N^3 in the case of T) one-dimensional irreducible representations, as discussed in Sect. 4.2. These are denoted as

$$\Gamma_{\mathrm{T}}^{\{\bar{n}_i\}}(\vec{B}) = \prod_{i=1}^{3} \exp\left[\mathrm{i}\frac{2\pi}{N} n_i \cdot \bar{n}_i\right] ,$$

where the triple of numbers $\bar{n}_i$ correspond to our usual label p for an irreducible representation. Alternatively we can introduce the reciprocal lattice with the basis vectors $\vec{g}_i$, for which holds

$$\vec{g}_i \cdot \vec{b}_j = 2\pi\delta_{i,j} . \tag{13.1}$$

Explicitly these vectors can be constructed with the formula

$$\vec{g}_i \equiv \frac{2\pi}{V}\vec{b}_k \times \vec{b}_l \quad , \quad V \equiv \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) \tag{13.2}$$

where (i, k, l) are arranged cyclically (see Exercise 1). Instead of the numbers $\bar{n}_i$ one usually defines *momentum space* vectors

$$\vec{k} = \sum_i k_i \cdot \vec{g}_i \tag{13.3}$$

with

$$k_i \equiv \frac{\bar{n}_i}{N} \quad (\bar{n}_i = 0, 1, \ldots, N-1) \tag{13.4}$$

to denote the representations. Thus we can write the irreducible representations as

$$\Gamma_{\mathrm{T}}^{\vec{k}}(\vec{B}) = \exp\left[\mathrm{i}\vec{k} \cdot \vec{B}\right] . \tag{13.5}$$

In the following, we need a statement on the reciprocal lattice vectors: for the vectors

$$\vec{G}(\bar{n}_1, \bar{n}_2, \bar{n}_3) = \sum_{i=1}^{3} \bar{n}_i \cdot \vec{g}_i \tag{13.6}$$

of the reciprocal lattice (and only for these!) holds

$$\vec{B} \cdot \vec{G} = 2\pi \cdot \underbrace{m}_{\in\mathbb{Z}} , \tag{13.7}$$

for all vectors $\vec{B}$ of the Bravais lattice.

Proof If $\vec{B}'$ is given as in (13.6), then

$$\vec{B} \cdot \vec{G} \overset{(13.1)}{=} 2\pi \sum_{i=1}^{3} n_i \cdot \bar{n}_i \ .$$

The sum on the right-hand side can be integer for all n_i only if the $\bar{n}_i$ are also integer, which proves the statement.

The reciprocal lattice belongs to the same crystal system as the corresponding Bravais lattice, i.e. it has the same point group G_0, because if $\tilde{D} \in G_0$, then

$$(\tilde{D} \cdot \vec{G}) \cdot \vec{B} = \vec{G} \cdot (\tilde{D}^{-1} \cdot \vec{B}) = 2\pi \cdot m \ .$$

Here we use the fact that $\tilde{D}^{-1} \cdot \vec{B}$ also belongs to the Bravais lattice. This leads to the conclusion that $\tilde{D} \cdot \vec{G}$ must also belong to the reciprocal lattice, hence $\tilde{D}$ is an element of the point group of the reciprocal lattice. However, the reciprocal lattice generally does not possess the same space group as the corresponding Bravais lattice. For instance, a cubic body-centered Bravais lattice has a cubic face-centered reciprocal lattice and vice versa (as demonstrated in Exercise 2).

The irreducible representations of a translation group T are not affected by translations in momentum space of a reciprocal lattice vector $\vec{B}'$, since

$$\Gamma_{\mathrm{T}}^{\vec{k}+\vec{G}}(\vec{B}) = \exp\left[\mathrm{i}(\vec{k}+\vec{G}) \cdot \vec{B}\right] \overset{(13.7)}{=} \exp\left[\mathrm{i}\vec{k} \cdot \vec{B}\right] = \Gamma_{\mathrm{T}}^{\vec{k}}(\vec{B}) \ .$$

Instead of the vectors $\vec{k}$ introduced in (13.3), in the following we will work with vectors from the *Brillouin zone*, i.e. with numbers

$$\bar{n}_i = -\frac{N}{2} + 1, -\frac{N}{2} + 1, \ldots, \frac{N}{2} \tag{13.8}$$

in the vectors (13.3) (defined with (13.4)), where we have made the unproblematic assumption that N is even.

13.2 The Irreducible Representations of Symmorphic Space Groups

In this section, we will analyze the irreducible representations of symmorphic space groups. This is mathematically similar to the problem discussed in Sect. 11.5, where we examined the irreducible representations of double groups: Given a group G with a normal sub-group H (in this case T) whose irreducible representations are all known (as discussed in Sect. 13.1), there exists a general method to construct irreducible representations of G in this case. However, we will not delve into the details of this general mathematical method here and instead solely focus on the irreducible

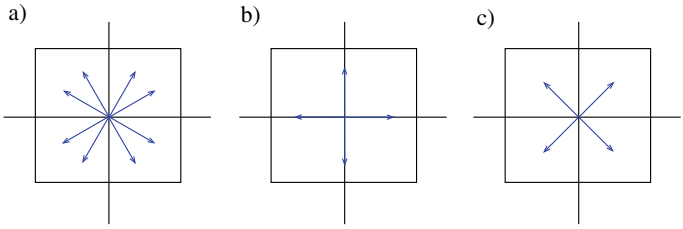

Fig. 13.1 Three examples of a star of $\vec{k}$ in a quadratic Brillouin zone. The left star is in a general position

representations of space groups. To this end, we will provide the explicit form of the representation matrices in this section and then demonstrate their representation properties, irreducibility, and completeness.

For each vector from the Brillouin zone, one defines the *star of* $\vec{k}$ as the set $\{\vec{k}_i\}$ of all vectors that can be mapped on each other via a matrix $\tilde{D} \in G_0$. Three examples of such stars can be found in Fig. 13.1. Obviously a star has at most g_0 elements if g_0 is the number of elements in G_0. A star with g_0 elements is said to be *in general position*. This applies, for example, to star a) in Fig. 13.1. All stars in non-general positions have at least one matrix $\tilde{D} \in G_0$ with $\tilde{D} \cdot \vec{k} = \vec{k}$. In the two stars b), c) in Fig. 13.1 these are the matrices $\tilde{D}$ of the respective mirror planes.

We can now formulate the crucial statement in this context: For every star of $\vec{k}$ (with $\vec{k} \neq \vec{0}$) there is exactly one g_0-dimensional irreducible representation of a space group. Only at the Γ-point, the situation is different. There too, however, the sum of the dimensions of the irreducible representations equals the dimension g_0 of G_0. In what follows we shall consider stars in general and non-general positions one after another.[1]

13.2.1 Irreducible Representations of a Star in General Position

For every star of $\vec{k}$ in general position there exists exactly one g_0-dimensional irreducible representation of a space group. We define the g_0 elements of a star $\vec{k}$ by

$$\vec{k}_i = \tilde{D}_i \cdot \vec{k} \quad (i = 1, \ldots, g_0) \; .$$

Then an irreducible representation of the space group is given by the g_0-dimensional matrices

$$\Gamma_{i,j}(\{\tilde{D}|\vec{R}\}) = \exp\left[\mathrm{i}\vec{k}_i \cdot \vec{R}\right] \cdot \Delta_{i,j}(\tilde{D}) \; , \tag{13.9}$$

[1] This procedure has more didactic reasons, since the results in Sect. 13.2.1 are included as a special case in the more complicated considerations in Sect. 13.2.2.

where

$$\Delta_{i,j}(\tilde{D}) = \begin{cases} 1 \text{ if } & \langle \vec{k}_i | \tilde{D} | \vec{k}_j \rangle = \vec{k}^2 \\ 0 & \text{otherwise} \end{cases} .$$

Note that for the non-vanishing matrix elements $\Delta_{i,j}(\tilde{D})$, the following applies

$$\vec{k}^2 = \langle \vec{k}_i | \tilde{D} | \vec{k}_j \rangle = \langle \vec{k} | \tilde{D}_i^{-1} \cdot \tilde{D} \cdot \tilde{D}_j | \vec{k} \rangle \quad \Rightarrow \quad \tilde{1} = \tilde{D}_i^{-1} \cdot \tilde{D} \cdot \tilde{D}_j \ .$$

The representation matrices (13.9) have exactly one finite element in each row or column. In particular, for $i = j$ we find

$$\Gamma_{i,j}(\{\tilde{1}|\vec{R}\}) = \delta_{i,j} \exp[\mathrm{i}\vec{k}_i \cdot \vec{R}] = \delta_{i,j} \Gamma_{\mathrm{T}}^{\vec{k}_i}(\vec{R})$$

which reproduces the irreducible representations of the translation group given in (13.5).

Proof (*of the representation property and the irreducibility of* (13.9))

(i) Representation property: With matrices $\tilde{D}$, $\tilde{D}' \in G_0$ and vectors $\vec{R}$, $\vec{R}'$ from the translation group it is

$$\{\tilde{D}|\vec{R}\} \cdot \{\tilde{D}'|\vec{R}'\} = \{\tilde{D} \cdot \tilde{D}'|\tilde{D} \cdot \vec{R}' + \vec{R}\} \in G \ .$$

We now insert the right hand side of this equation into the representation definition (13.9),

$$\Gamma_{i,j}(\{\tilde{D} \cdot \tilde{D}'|\tilde{D} \cdot \vec{R}' + \vec{R}\}) = \exp[\vec{k}_i \cdot \vec{R} + \mathrm{i}\vec{k}_i \cdot (\tilde{D} \cdot \vec{R}')] \Delta_{i,j}(\tilde{D} \cdot \tilde{D}') \ . \quad (13.10)$$

The second factor on the right hand side can be written as

$$\begin{aligned} \Delta_{i,j}(\tilde{D} \cdot \tilde{D}') &= \begin{cases} 1 \text{ if } & \tilde{D}_i = \tilde{D} \cdot \tilde{D}' \cdot \tilde{D}_j \\ 0 & \text{otherwise} \end{cases} \\ &= \sum_l \Delta_{i,l}(\tilde{D}) \cdot \Delta_{l,j}(\tilde{D}') \ . \end{aligned} \quad (13.11)$$

In the second line, we have exploited the fact that the two factors $\Delta_{i,l}(\tilde{D})$ and $\Delta_{l,j}(\tilde{D})$ are non-zero only if

$$\tilde{D}_i = \tilde{D} \cdot \tilde{D}_l \quad (13.12)$$

and

$$\tilde{D}_l = \tilde{D}' \cdot \tilde{D}_j \quad (13.13)$$

respectively. For the product of the two to be non-zero, both conditions must be satisfied. Substituting (13.13) into (13.12) then gives exactly the condition in (13.11). Now we are able to evaluate the right hand side of (13.10),

$$\begin{aligned}\Gamma_{i,j}(\{\tilde{D}\cdot\tilde{D}'|\tilde{D}\cdot\vec{R}'+\vec{R}\}) &= \sum_l \exp[\mathrm{i}\vec{k}_i\cdot\vec{R}]\exp[\underbrace{\mathrm{i}\vec{k}_i\cdot(\tilde{D}\cdot\vec{R}')}_{\overset{(13.12)}{=}(\tilde{D}\cdot\vec{k}_l)\cdot(\tilde{D}\cdot\vec{R}')=\vec{k}_l\cdot\vec{R}'}]\Delta_{i,l}(\tilde{D})\cdot\Delta_{l,j}(\tilde{D}) \\ &= \sum_l \Gamma_{i,l}(\{\tilde{D}|\vec{R}\})\Gamma_{l,j}(\{\tilde{D}'|\vec{R}'\}) \quad \surd \end{aligned} \tag{13.14}$$

(ii) Irreducibility: To prove the irreducibility of the representation (13.9), we use the criterion from Sect. 5.2.3, i.e. the fact that a representation is irreducible exactly if

$$\sum_a |\chi(a)|^2 = g\ . \tag{13.15}$$

In our space groups, the number of group elements is equal to

$$g = N^3 g_0\ .$$

The left-hand side of (13.15) becomes for the space groups

$$\sum_{\vec{R},\tilde{D}} \Big|\sum_i \Gamma_{i,i}(\{\tilde{D}|\vec{R}\})\Big|^2 = \sum_{\vec{R}} \Big|\sum_i \exp[\mathrm{i}\vec{k}_i\cdot\vec{R}]\Big|^2$$

because

$$\Delta_{i,i}(\tilde{D}) = \delta_{\tilde{D},\tilde{1}}\ .$$

This leads to

$$\sum_{\vec{R}} \Big|\sum_i \exp[\mathrm{i}\vec{k}_i\cdot\vec{R}]\Big|^2 = \sum_{i,j} \underbrace{\sum_{\vec{R}} \exp[\mathrm{i}(\vec{k}_i-\vec{k}_j)\cdot\vec{R}]}_{=N^3\cdot\delta_{i,j}} = N^3 g_0\ . \quad \surd$$

13.2.2 *Irreducible Representations of a Star in Non-general Position*

From a thermodynamic point of view, one could argue that the weight of stars in non-general position vanishes in the thermodynamic limit. In experimental physics such stars are nevertheless of importance, for example in the analysis of ARPES[2] exper-

[2] Angle-resolved photoemission spectroscopy.

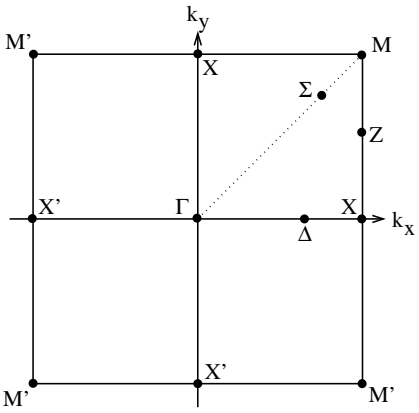

Fig. 13.2 The Brillouin zone of a quadratic lattice with certain $\vec{k}$ in a non-general position

iments which measures the band structure of metals usually along high-symmetry lines. Therefore, we will also consider in the following the stars in non-general position.

If a $\vec{k}$-point is not in a general position, then there exist $\tilde{D} \in G_0$ for which holds

$$\tilde{D} \cdot \vec{k} = \vec{k} + \vec{B}' \ ,$$

with some reciprocal lattice vector $\vec{B}'$. These elements form a sub-group $G_0(\vec{k})$ of G_0 that shall have the order $q_{\vec{k}}$. While for all $\vec{k}$ inside the Brillouin zone it is $\vec{B}' = \vec{0}$, a vector $\vec{B}' \neq \vec{0}$ may be required for $\vec{k}$-points at the edge of the Brillouin zone. This can be seen, for example, in the Brillouin zone of a square lattice in Fig. 13.2. If one mirrors the M point, e.g. at the axis $k_y = 0$, a reciprocal lattice vector is needed to end up at M again.

At the Γ-*point* ($\vec{k} = \vec{0}$) we have obviously $G_0(\vec{0}) = G_0$, whereas for a star in general position it is $G_0(\vec{k}) = C_1 = \{E\}$. For the other examples of $\vec{k}$-points in non-general position in Fig. 13.2 the point groups $G_0(\vec{k})$ are

$$\begin{aligned} G_0(\Gamma) &= C_{4v} \ , \\ G_0(\Sigma) &= G_0(\Delta) = G_0(Z) = C_s \ , \\ G_0(X) &= C_{2v} \ , \\ G_0(M) &= C_{4v} \ . \end{aligned}$$

Let the $g_{\vec{k}}$ elements of a star of $\vec{k}$ be given again by

$$\vec{k}_i = \tilde{D}_i \cdot \vec{k} \ , \quad (i = 1, \ldots, g_{\vec{k}} \ ; \ \tilde{D}_1 \equiv \tilde{1})$$

and let the following hold for the representants $\tilde{D}_i$:

$$\tilde{D}_i^{-1} \cdot \tilde{D}_j \in G_0(\vec{k}) \quad \forall i \neq j \ .$$

This restriction modifies our earlier definition of a star of $\vec{k}$ for the $\vec{k}$-points located at the edge of the Brillouin zone. For example, the star of the X point in Fig. 13.2 consists of only two vectors, since the two points X' are not in the Brillouin zone, see (13.8). Let, furthermore, $R^{\vec{k}}$ be a $p_{\vec{k}}$-dimensional irreducible representation of $G_0(\vec{k})$. Then one irreducible $g_{\vec{k}} \cdot p_{\vec{k}}$-dimensional representation belonging to the star of $\vec{k}$ is given by

$$\Gamma_{(i\lambda),(j\lambda')}(\{\tilde{D}|\vec{R}\}) = \exp\left[\mathrm{i}\vec{k}_i \cdot \vec{R}\right] \cdot \Delta_{i,j}(\tilde{D}) \cdot R^{\vec{k}}_{\lambda,\lambda'}(\tilde{D}_i^{-1} \cdot \tilde{D} \cdot \tilde{D}_j) \ , \tag{13.16}$$

where $\Delta_{i,j}(\tilde{D}) = (0, 1)$ has been defined in (13.11). If $\Delta_{i,j}(\tilde{D}) \neq 0$, it follows

$$\langle \vec{k}_i | \tilde{D} | \vec{k}_j \rangle = \vec{k}^2 \quad \Leftrightarrow \langle \vec{k} | \tilde{D}_i^{-1} \cdot \tilde{D} \cdot \tilde{D}_j | \vec{k} \rangle = \vec{k}^2 \ ,$$

which means that $\tilde{D}_i^{-1} \cdot \tilde{D} \cdot \tilde{D}_j \in G_0(\vec{k})$. Therefore, the argument of $R^{\vec{k}}_{\lambda,\lambda'}$ in (13.16) is always meaningful. Again (with fixed λ, λ') with respect to i, j in each column/row only one element is not equal to zero, because suppose there are $j \neq j'$ with $\Delta_{i,j}(\tilde{D}) = \Delta_{i,j'}(\tilde{D}) = 1$ in (13.16). Then,

$$\left.\begin{matrix} \tilde{D}_i^{-1} \cdot \tilde{D} \cdot \tilde{D}_j \\ \tilde{D}_i^{-1} \cdot \tilde{D} \cdot \tilde{D}_{j'} \end{matrix}\right\} \in G_0(\vec{k}) \ .$$

This, however, would also mean that

$$\left(\tilde{D}_i^{-1} \cdot \tilde{D} \cdot \tilde{D}_j\right)^{-1} \cdot \left(\tilde{D}_i^{-1} \cdot \tilde{D} \cdot \tilde{D}_{j'}\right) = \left(\tilde{D}_j^{-1} \cdot \tilde{D}^{-1} \cdot \tilde{D}_i\right) \cdot \left(\tilde{D}_i^{-1} \cdot \tilde{D} \cdot \tilde{D}_{j'}\right) = \tilde{D}_j^{-1} \cdot \tilde{D}_{j'} \in G_0(\vec{k}) \ .$$

which was explicitly excluded in the definition of a star of $\vec{k}$. So, written as a matrix, (13.16) has a similar form as in Sect. 13.2.1, if we replace $\Delta_{i,j} = 1$ by $\tilde{R}^{\vec{k}}(\tilde{D})$.

Proof

(i) The proof is very similar to that in Sect. 13.2.1. The resulting exponential function can be evaluated at the end in a similar way as in (13.14). Therefore we only have to show here that

$$\Delta_{i,j}(\tilde{D} \cdot \tilde{D}') \cdot R^{\vec{k}}_{\lambda,\lambda'}(\tilde{D}_i^{-1} \cdot \tilde{D} \cdot \tilde{D}' \cdot \tilde{D}_j) = \begin{cases} R^{\vec{k}}_{\lambda,\lambda'}(\ldots) \text{ if } & \tilde{D}_i^{-1} \cdot \tilde{D} \cdot \tilde{D}' \cdot \tilde{D}_j \in G_0(\vec{k}) \\ 0 & \text{otherwise} \end{cases}$$

$$= \sum_{l,\mu} \left[\Delta_{i,l}(\tilde{D}) \cdot R^{\vec{k}}_{\lambda,\mu}(\tilde{D}_i^{-1} \cdot \tilde{D} \cdot \tilde{D}_l)\right] \left[\Delta_{l,j}(\tilde{D}) \cdot R^{\vec{k}}_{\mu,\lambda'}(\tilde{D}_l^{-1} \cdot \tilde{D}' \cdot \tilde{D}_j)\right] \tag{13.17}$$

Since $\vec{R}^{\vec{k}}$ is a representation, the sum over μ in (13.17) leads to

$$(13.17) = \left[\sum_l \Delta_{i,l}(\tilde{D}) \cdot \Delta_{l,j}(\tilde{D}')\right] R^{\vec{k}}_{\lambda,\lambda'}(\tilde{D}_i^{-1} \cdot \tilde{D} \cdot \tilde{D}' \cdot \tilde{D}_j)$$

The sum over l only makes a contribution if both factors are $\neq 0$, i.e. if

$$\begin{matrix} \tilde{D}_i^{-1} \cdot \tilde{D} \cdot \tilde{D}_l \in G_0(\vec{k}) \\ \tilde{D}_l^{-1} \cdot \tilde{D}' \cdot \tilde{D}_j \in G_0(\vec{k}) \end{matrix} \quad \Rightarrow \tilde{D}_i^{-1} \cdot \tilde{D} \cdot \tilde{D}' \cdot \tilde{D}_j \in G_0(\vec{k})$$

This is exactly the condition in (13.17), i.e. it is

$$\sum_l \Delta_{i,l}(\tilde{D}) \cdot \Delta_{l,j}(\tilde{D}') = \Delta_{i,j}(\tilde{D} \cdot \tilde{D}') \quad \surd$$

(ii) To prove the irreducibility, we use again the criterion (13.15). For this, we need the trace of the matrix (13.16),

$$\mathrm{Tr}\left[\tilde{\Gamma}(\{\tilde{D}|\vec{R}\})\right] = \sum_i \exp\left[\mathrm{i}\vec{k}_i \cdot \vec{R}\right] \cdot \Delta_{i,i}(\tilde{D}) \cdot \underbrace{\chi^{\vec{k}}(\tilde{D}_i^{-1} \cdot \tilde{D} \cdot \tilde{D}_i)}_{\equiv \sum_\lambda R^{\vec{k}}_{\lambda,\lambda}(\tilde{D}_i^{-1} \cdot \tilde{D} \cdot \tilde{D}_j)} . \qquad (13.18)$$

As seen above, it is $\Delta_{i,i}(\tilde{D}) \neq 0$ if $\tilde{D}_i^{-1} \cdot \tilde{D} \cdot \tilde{D}_i \in G_0(\vec{k})$, from which it follows that $\tilde{D} \in G_0(\vec{k}_i)$ and we can replace $\chi^{\vec{k}}(\tilde{D}_i^{-1} \cdot \tilde{D} \cdot \tilde{D}_i)$ in (13.18) by $\chi^{\vec{k}_i}(\tilde{D})$. The criterion (13.15) then leads to

$$\begin{aligned} &\sum_{\tilde{D}} \sum_{\vec{R}} \left| \sum_i \exp\left[\mathrm{i}\vec{k}_i \cdot \vec{R}\right] \cdot \Delta_{i,i}(\tilde{D}) \cdot \chi^{\vec{k}_i}(\tilde{D}) \right|^2 \\ &= \sum_{\tilde{D}} \sum_{i,j} \underbrace{\left(\sum_{\vec{R}} \exp\left[\mathrm{i}(\vec{k}_i - \vec{k}_j) \cdot \vec{R}\right] \right)}_{= N^3 \delta_{i,j}} \Delta_{i,i}(\tilde{D}) \cdot \Delta_{j,j}(\tilde{D}) \left| \chi^{\vec{k}_i}(\tilde{D}) \right|^2 \\ &= N^3 \sum_i \underbrace{\sum_{\tilde{D} \in G_0(\vec{k}_i)} \cdot \left| \chi^{\vec{k}_i}(\tilde{D}) \right|^2}_{\overset{(13.15)}{=} q_{\vec{k}}} = N^3 q_{\vec{k}} \underbrace{\sum_i}_{g_{\vec{k}}} = N^3 \underbrace{q_{\vec{k}} g_{\vec{k}}}_{= g_0} = g \cdot \surd \end{aligned}$$

(iii) The question remains to be answered whether the set of irreducible representations found in Sects. 13.2.1 and 13.2.2 is complete. To answer this question, we

can use (4.20). The sum over p in (4.20) is, in the case of the space groups, a sum over all stars, and for each star the sum over all irreducible representations $R_l^{\vec{k}}$ (with dimension $p_{\vec{k}}^l$) of $G_0(\vec{k})$,

$$g = N^3 g_0 \stackrel{?}{=} \sum_{\text{stars}} \sum_{l} (g_{\vec{k}} p_{\vec{k}}^l)^2 = \sum_{\text{stars}} g_{\vec{k}}^2 \underbrace{\sum_{p} (p_{\vec{k}}^l)^2}_{\stackrel{(13.15)}{=} q_{\vec{k}}} = g_0 \underbrace{\sum_{\text{stars}} g_{\vec{k}}}_{=N^3} = N^3 g_0 \quad \cdot\surd$$

13.3 Spectrum of a Hamiltonian with Space Group Symmetry

Because of the quantum mechanical postulate in Sect. 6.3.3 it is now clear that eigenstates $|\Psi\rangle$ in a solid can be classified as follows

$$|\Psi\rangle = |\vec{k}, \gamma\rangle \ ,$$

where $\vec{k}$ is in the Brillouin zone and $\gamma = 1, \ldots, \infty$ is usually called the *band index*. All states of a band γ belonging to a star of $\vec{k}$ are degenerate. For stars in a general position there is no degeneracy at any $\vec{k}$-point. This is different for stars in non-general position, where the degeneracy at a $\vec{k}$-point is given by the dimension $d_{\vec{k}}$ of the representation $\bar{R}^{\vec{k}}$.

The Γ-point ($\vec{k} = \vec{0}$) is a special case for several reasons: The star of $\vec{k} = \vec{0}$ consists of only one element and it is $G_0(\vec{0}) = G_0$, i.e. the irreducible representations at the Γ-point are exactly those of the point group G_0. Furthermore, eigenstates at the gamma point (and only there) are translation invariant (see (13.16)) i.e.

$$\hat{T}_{\{\tilde{1}|\vec{R}\}} |\vec{0}, \gamma\rangle = |\vec{0}, \gamma\rangle \ .$$

Exercises

1. Show that the basis vectors $\vec{b}_i'$ from (13.1) are given by (13.2).
2. Show that a cubic body-centered Bravais lattice has a cubic face-centered reciprocal lattice, and vice versa.

Chapter 14
Particles in Periodic Potentials

Non-interacting electrons in a periodic potential are an important example of a physical system with a space group symmetry. Due to the lack of interactions among the electrons, one only needs to solve the eigenvalue problem of a single electron in that potential. The energy levels are subsequently filled following the Pauli exclusion principle, and ignoring the spin-orbit interaction also allows us to disregard the electron's spin.

Section 14.1 focuses on the Schrödinger equation of the system and derives the well-known Bloch theorem with group-theoretical arguments. We explain in Sect. 14.2 why determining the eigenstates in a certain part of the Brillouin zone is sufficient, since all other eigenstates can be derived from these. The resulting band structures satisfy compatibility conditions along high-symmetry lines, which we discuss in Sect. 14.3 using our perturbation theory considerations from Chap. 8. Furthermore, we explore two methods for perturbatively creating the Hamiltonian of electrons in a solid. In Sect. 14.4, we gradually introduce the periodic potential by starting with free particles. In an alternative way, tight-binding models are derived from the combination of atoms into solids, which is explored in Sect. 14.5.

14.1 Schrödinger Equation, Bloch Theorem

We consider the eigenvalue equation

$$\hat{H}\Psi(\vec{r}) = E\Psi(\vec{r}) \tag{14.1}$$

with the single-particle Hamiltonian

$$\hat{H} = -\frac{1}{2m}\hat{\Delta} + V(\hat{\vec{r}}) \ ,$$

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and a potential

$$V(\vec{r}) = -\sum_i e^2 \frac{Z_i}{|\vec{r} - \vec{B}_i|} ,$$

where $\vec{B}_i$ is the location of the nucleus i and Z_i is its nuclear charge number. The potential $V(\vec{r})$ is invariant under the transformations of a space group $G = \{\{\tilde{D}|\vec{B}\}\}$, i.e.

$$V(\tilde{D} \cdot \hat{\vec{r}} + \vec{B}) = V(\hat{\vec{r}}) \quad \forall \{\tilde{D}|\vec{B}\} .$$

Then, from Chap. 13, we know that each eigenstate of $\hat{H}$ can be assigned a vector $\vec{k}$ from the Brillouin zone and we know that the behavior of this state under lattice vector translations $\vec{B}$ (see (13.16)) is given by

$$\Psi_{\vec{k}}(\vec{r} + \vec{B}) = e^{i\vec{k}\cdot\vec{B}} \cdot \Psi_{\vec{k}}(\vec{r}) .$$

This means in particular that

$$|\Psi_{\vec{k}}(\vec{r} + \vec{B})|^2 = |\Psi_{\vec{k}}(\vec{r})|^2 ,$$

which is why we can write $\Psi_{\vec{k}}(\vec{r})$ as

$$\Psi_{\vec{k}}(\vec{r}) = e^{i\varphi_{\vec{k}}(\vec{r})} \cdot v_{\vec{k}}(\vec{r}) .$$

Here, $\varphi_{\vec{k}}(\vec{r}) \in \mathbb{R}$, and

$$\begin{aligned} \varphi_{\vec{k}}(\vec{r} + \vec{B}) &= \varphi_{\vec{k}}(\vec{r}) + \vec{k} \cdot \vec{B} \quad \Rightarrow \quad \varphi_{\vec{k}}(\vec{r}) = \eta_{\vec{k}}(\vec{r}) + \vec{k} \cdot \vec{r} , \\ v_{\vec{k}}(\vec{r} + \vec{B}) &= v_{\vec{k}}(\vec{r}) , \\ \eta_{\vec{k}}(\vec{r} + \vec{B}) &= \eta_{\vec{k}}(\vec{r}) . \end{aligned}$$

In this way, we reproduce the well known *Bloch theorem* in a group-theoretical way,

$$\Psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \cdot u_{\vec{k}}(\vec{r}) , \tag{14.2}$$

where

$$u_{\vec{k}}(\vec{r}) \equiv \exp\left[i\eta_{\vec{k}}(\vec{r})\right] \cdot v_{\vec{k}}(\vec{r}) ,$$

is translation invariant, $u_{\vec{k}}(\vec{r} + \vec{B}) = u_{\vec{k}}(\vec{r})$.

Substituting the wave function (14.2) into (14.1) yields the eigenvalue equation

$$\hat{H}_{\vec{k}} u_{\vec{k}}(\vec{r}) = E_{\vec{k}} u_{\vec{k}}(\vec{r}) \tag{14.3}$$

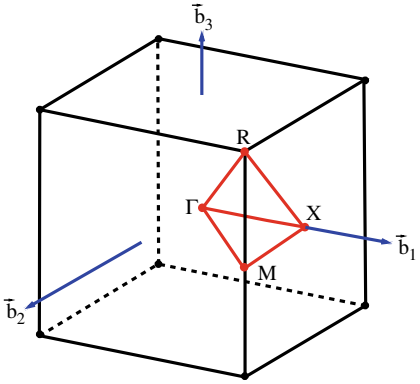

Fig. 14.1 Irreducible part of a simple cubic Brillouin zone

for $u_{\vec{k}}(\vec{r})$ with the $\vec{k}$-dependent Hamiltonian

$$\hat{H}_{\vec{k}} = -\frac{1}{2m}\left(\Delta + 2\mathrm{i}\vec{k}\cdot\vec{\nabla} - \vec{k}^2\right) + V(\hat{\vec{r}}) \ . \tag{14.4}$$

In the following, we consider $\vec{k}$ as a constant vector in the spatial eigenvalue (14.3). The space group of $\hat{H}_{\vec{k}}$ is

$$G(\vec{k}) \equiv \{\{\tilde{D}|\vec{B}\}\}$$

with $\tilde{D} \in G_0(\vec{k})$ (as defined in Sect. 13.2.2) and $\vec{B} \in T$ is a sub-group of G (for $\vec{k} \neq \vec{0}$). The translation invariant eigenstates $u_{\vec{k}}(\vec{r})$ (with respect to lattice vectors $\vec{B}$) of $\hat{H}_{\vec{k}}$ belong to its Γ-point (see Sect. 13.3).[1] This means that the states are irreducible representation functions of the point group of $G(\vec{k})$, i.e. $G_0(\vec{k})$. However, these are exactly the states $u_{\vec{k}}(\vec{r})$. Therefore, they have a degeneracy $d_p(\vec{k})$ of that representation's ($\bar{\Gamma}^p$) dimension and it is

$$\hat{T}_{\tilde{D}} \cdot u_{\vec{k},\alpha}(\vec{r}) = \sum_{\alpha'} \Gamma^p_{\alpha',\alpha} \cdot u_{\vec{k},\alpha'} \qquad (\alpha = a, \ldots, d_p(\vec{k})) \ .$$

for all $\tilde{D} \in G_0(\vec{k})$.

14.2 Irreducible Part of the Brillouin Zone

We will now demonstrate explicitly that the eigenstates (14.2) transform in the same way as the irreducible representations discussed in Chap. 13.

[1] Knowing that this point can be confusing when you first read it, here is the following note: The Hamiltonian $\hat{H}_{\vec{k}}$ has eigenstates $U_{\vec{k}'}(\vec{r})$, whose wave vector $\vec{k}'$ has nothing to do with the constant vector $\vec{k}$ in $\hat{H}_{\vec{k}}$. The Γ-point then means the vector $\vec{k}' = \vec{0}$, i.e. it is $U_{\vec{0}}(\vec{r}) = u_{\vec{k}}(\vec{r})$.

An *irreducible part of the Brillouin zone* refers to a portion of the Brillouin zone from which all other points can be generated through transformations $\tilde{D} \in G_0$. For instance, in a simple cubic lattice, the red region depicted in Fig. 14.1 is irreducible. If we know the eigenstates $\Psi_{\vec{k},\gamma}(\vec{r})$ of $\hat{H}(\vec{k})$ in the irreducible Brillouin zone, we can determine all eigenstates of $\hat{H}(\vec{k})$ through *star operations* $\hat{T}_{\tilde{D}_\gamma}$ $(\gamma = 1, \ldots, d_p(\vec{k}))$, see Chap. 1: Let the eigenstates

$$\Psi_{\vec{k},\gamma}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k},\gamma}(\vec{r})$$

be given with a fixed $\vec{k}$ in the irreducible Brillouin zone and energies $E_{\vec{k}}$ with $\gamma = 1, \ldots, d_p(\vec{k})$. If the star of $\vec{k}$ is again given by the representants $\tilde{D}_i$, i.e. $\vec{k}_i = \tilde{D}_i \cdot \vec{k}$ then the states

$$|\Psi_{\vec{k}_i,\gamma}\rangle \equiv \hat{T}_{\tilde{D}_i} \cdot |\Psi_{\vec{k},\gamma}\rangle \ , \tag{14.5}$$

form an irreducible representation space of the space group G and thus an eigenspace of $\hat{H}$ to the energy $E_{\vec{k}}$.

Proof We consider successively the effect of rotation and translation operators on the states (14.5):

(i) Behavior under rotations:

$$\begin{aligned} \hat{T}_{\tilde{D}}|\Psi_{\vec{k}_i,\gamma}\rangle &\overset{(14.5)}{=} \hat{T}_{\tilde{D}\cdot\tilde{D}_i}|\Psi_{\vec{k},\gamma}\rangle \\ &= \sum_j \Delta_{i,j}(\tilde{D}) \cdot \hat{T}_{\tilde{D}_j} \cdot \hat{T}_{\tilde{D}_j^{-1}\cdot\tilde{D}\cdot\tilde{D}_i}|\Psi_{\vec{k},\gamma}\rangle \end{aligned}$$

In the second line we have used that $\Delta_{i,j}(\tilde{D})$ is non-zero (and then 1) only for one term in the sum over j, namely when $\tilde{D}_j^{-1} \cdot \tilde{D} \cdot \tilde{D}_i \in G_0(\vec{k})$. For this transformation in $G_0(\vec{k})$ is

$$\hat{T}_{\tilde{D}_j^{-1}\cdot\tilde{D}\cdot\tilde{D}_i}|\Psi_{\vec{k},\gamma}\rangle = \sum_{\gamma'} R^{\vec{k}}_{\gamma',\gamma}(\tilde{D}_j^{-1} \cdot \tilde{D} \cdot \tilde{D}_i)|\Psi_{\vec{k},\gamma'}\rangle \ .$$

Hence, we obtain

$$\begin{aligned} \hat{T}_{\tilde{D}}|\Psi_{\vec{k}_i,\gamma}\rangle &= \sum_j \Delta_{i,j}(\tilde{D}) \sum_{\gamma'} R^{\vec{k}}_{\gamma',\gamma}(\tilde{D}_j^{-1} \cdot \tilde{D} \cdot \tilde{D}_i) \cdot \hat{T}_{\tilde{D}_j}|\Psi_{\vec{k},\gamma'}\rangle \\ &= \sum_j \Delta_{i,j}(\tilde{D}) \sum_{\gamma'} R^{\vec{k}}_{\gamma',\gamma}(\tilde{D}_j^{-1} \cdot \tilde{D} \cdot \tilde{D}_i)|\Psi_{\vec{k}_j,\gamma'}\rangle \ . \end{aligned} \tag{14.6}$$

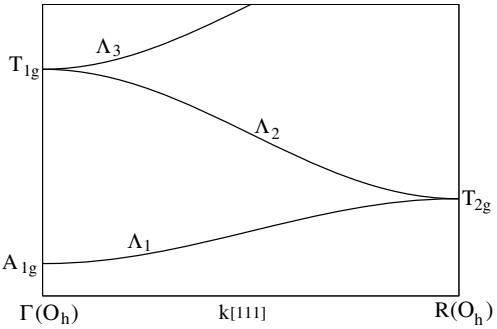

Fig. 14.2 A fictitious band structure between the Γ and the R point of a cubic lattice to illustrate the compatibility conditions

(ii) Behavior under translations:

$$\begin{aligned}\hat{T}_{\vec{B}}|\Psi_{\vec{k}_i,\gamma}\rangle &= \underbrace{\hat{T}_{\vec{B}}\cdot\hat{T}_{\hat{T}_{\tilde{D}_i}}}_{=\hat{T}_{\tilde{D}_i}\cdot\hat{T}_{\{\tilde{1}|\tilde{D}_i^{-1}\cdot\vec{B}\}}}|\Psi_{\vec{k},\gamma}\rangle \\ &= \hat{T}_{\tilde{D}_i}\cdot\exp\left[\mathrm{i}\vec{k}\cdot(\tilde{D}_i^{-1}\cdot\vec{k}\right]|\Psi_{\vec{k},\gamma}\rangle \\ &= \exp\left[\mathrm{i}\vec{k}_i\cdot\vec{B}\right]|\Psi_{\vec{k}_i,\gamma}\rangle \qquad (14.7)\end{aligned}$$

With (14.6) and (14.7) we have shown that $|\Psi_{\vec{k}_i,\gamma}\rangle$ transforms like the irreducible representations in (13.16).

14.3 Compatibility Conditions

As a function of $\vec{k}$, the eigenspaces of (14.4) must evolve in a group theoretically well-defined way. Let $\hat{H}_{\vec{k}}$ be given, then in leading order in $\Delta\vec{k}$ it is

$$\hat{H}_{\vec{k}+\Delta\vec{k}} \approx \hat{H}_{\vec{k}} - \frac{\mathrm{i}}{m}\Delta\vec{k}\cdot\vec{\nabla}\ .$$

In the case of a small change in $\Delta\vec{k}$, the perturbative arguments discussed in Chap. 8 can be applied. Let $\Gamma^p_{\vec{k}}$ be the irreducible representation of an eigenspace at the point $\vec{k}$. If the symmetry group of $\hat{H}(\vec{k}+\Delta\vec{k})$ is a sub-group of $\hat{H}(\vec{k})$, then the eigenspaces of $\hat{H}(\vec{k}+\Delta\vec{k})$ can be obtained by the subdued representation of $\bar{\Gamma}^p(\vec{k})$. As a result, in band structures similar to those shown in Fig. 14.2, it is necessary to meet *compatibility conditions* if a band connects two points of high symmetry. For example, at the Γ and R points, the symmetry group is O_h, while the symmetry group C_{3v} is present along the connecting line $k[111]$. The splittings can then be determined using the correlation tables,

$$A_{1g} \to A_1$$
$$T_{1g} \to A_2 \oplus E$$
$$T_{2g} \to A_1 \oplus E$$

From this analysis we can predict, to what irreducible representation of C_{3v} the bands in Fig. 14.2 belong, namely

$$\Lambda_1 : A_1 \ ,$$
$$\Lambda_2 : E \ ,$$
$$\Lambda_2 : A_2 \ .$$

14.4 Solution of the Eigenvalue Problem with Plane Waves

In this section, we will explore a theoretical approach to study electrons in solids, in which we begin with free particles and then add the periodic potential perturbatively. Here, too, we will confirm our general results on the irreducible representations of the space groups from Chap. 13. The potential, denoted by $V(\vec{r})$, and the functions $u_{\vec{k}}(\vec{r})$ in (14.2) exhibit lattice translation invariance, allowing us to express them as a Fourier series,

$$\begin{Bmatrix} u_{\vec{k}}(\vec{r}) \\ V(\vec{r}) \end{Bmatrix} = \sum_{\vec{G}} \begin{Bmatrix} u_{\vec{k}}(\vec{G}) \\ V(\vec{G}) \end{Bmatrix} \exp(\mathrm{i}\vec{G} \cdot \vec{r}) \ ,$$

with the reciprocal lattice vectors $\vec{G}$ introduced in (13.6). When we substitute this Fourier expansion into the (14.3) we obtain the eigenvalue equation

$$\left[\frac{1}{2m} \left(\vec{G}^2 + 2\vec{G} \cdot \vec{k} + \vec{k}^2 \right) + V(\vec{G}) - E_{\vec{k}} \right] u_{\vec{k}}(\vec{G}) = - \sum_{\vec{G}'(\neq \vec{G})} V(\vec{G} - \vec{G}') u_{\vec{k}}(\vec{G}')$$

for the Fourier coefficients $u_{\vec{k}}(\vec{G})$. It is important to keep in mind at this stage, that the function we want to determine has $\vec{G}$ and $\vec{G}'$ as arguments, while $\vec{k}$ again is treated as a constant vector in the eigenvalue problem. Assuming that $V(\vec{G})$ is a small perturbation, standard arguments from perturbation theory can be applied with the unperturbed Schrödinger equation,

$$\hat{H}_0 u_{\vec{k}}(\vec{G}) \equiv \frac{1}{2m} \left(\vec{G}^2 + 2\vec{G} \cdot \vec{k} + \vec{k}^2 \right) u_{\vec{k}}(\vec{G}) = E_{\vec{k}} u_{\vec{k}}(\vec{G}) \ . \tag{14.8}$$

The solutions of this equation are evidently

$$u_{\vec{k},\vec{G}_0}(\vec{G}) = \delta_{\vec{G},\vec{G}_0} \ ,$$

Table 14.1 Character table of plane-wave representation spaces at the Γ-point

	O_h	E	$6C_4$	$3C_4^2$	$8C_3$	$6C_2'$	I	$3\sigma_h$	$6\sigma_d$	$8S_6$	$6S_4$
Γ_0:	$\vec{G}_0^2 = 0$	1	1	1	1	1	1	1	1	1	1
Γ_1:	$\vec{G}_0^2 = 1$	6	2	2	0	0	0	4	2	0	0
Γ_2:	$\vec{G}_0^2 = 2$	12	0	0	0	2	0	4	2	0	0

and have the following form in position space,

$$u_{\vec{k},\vec{G}_0}(\vec{r}) = e^{\mathrm{i}\vec{G}_0\cdot\vec{r}} \ .$$

If we put this result into (14.2), we find

$$\Psi_{\vec{k}+\vec{G}_0}(\vec{r}) = e^{\mathrm{i}(\vec{G}_0+\vec{k})\cdot\vec{r}} \ . \tag{14.9}$$

Since $\vec{G}_0 + \vec{k}$ can assume all values in $\mathbb{R}^3$, we reproduce the set of all plane waves of free particles, as expected.

Now, the question arises how the eigenspaces of $\hat{H}_0$ split when the potential $V(\vec{G})$ is switched on. We will focus on a simple cubic lattice and begin by examining the Γ-point with $\vec{k} = \vec{0}$. The degenerate eigenspaces of H_0 in this case are determined by the vectors $\vec{G}_0$ with equal lengths. The first three degenerate eigenspaces are:

$$\begin{aligned}
&\vec{G}_0^2 = 0 \rightarrow 1 \text{ state } \vec{G}_0 = (0,0,0)^T \ , \\
&\vec{G}_0^2 = 1 \rightarrow 6 \text{ states } \vec{G}_0 = (1,0,0)^T, \ldots, \vec{G}_0 = (0,0,-1)^T \ , \\
&\vec{G}_0^2 = 2 \rightarrow 12 \text{ states } \vec{G}_0 = (1,1,0)^T, \ldots, \vec{G}_0 = (0,-1,-1)^T \ .
\end{aligned} \tag{14.10}$$

At the Γ-point, the point group is O_h, and all three spaces in (14.10) correspond to reducible representation spaces of a representation denoted by $\Gamma^{\vec{G}_0^2}$ for this group. The character tables for these r representations are given in Table 14.1. To determine the irreducible components of these representations, (5.23) can be utilized, resulting in:

$$\begin{aligned}
\Gamma_0 &= A_{1\mathrm{g}} \ , \\
\Gamma_1 &= A_{1\mathrm{g}} + E_{\mathrm{g}} + T_{1\mathrm{u}} \ , \\
\Gamma_2 &= A_{1\mathrm{g}} + E_{\mathrm{g}} + T_{1\mathrm{u}} + T_{2\mathrm{g}} + T_{2\mathrm{u}} \ .
\end{aligned}$$

This provides the first nine representations that would occur at the Γ-point, at least for small values of $V(\vec{G})$. However, the energetic order of the representations of course is dependent on the specific form of $V(\vec{G})$. We will show numerical results below.

Before that, we can now also analyze the energy splitting for a non-vanishing $\vec{k}$. For a $\vec{k}$ vector in general position, already the eigenspaces of $\hat{H}_0$ are not degenerate, in

Table 14.2 Character table of plane-wave representation spaces for $\vec{k} = k\vec{e}_x$

	C_{4v}	E	$2C_4$	C_4^2	$2\sigma_v$	$2\sigma_d$
Γ_0:	$\vec{G}_=(0,0,0)$	1	1	1	1	1
Γ_1:	$\vec{G} = (m,0,0)[m = \pm 1]$	1	1	1	1	1
Γ_2:	$\{\vec{G} = (0,\pm 1,0), \vec{G} = (0,0,\pm 1)\}$	4	0	0	2	0
Γ_3:	$\{\vec{G} = (m,\pm 1,0), \vec{G} = (m,0,\pm 1)\}[m = \pm 1]$	4	0	0	2	0
Γ_4:	$\{\vec{G} = (0,\pm 1,\pm 1)\}$	4	0	0	0	2

agreement with our general results in Sect. 13.2.1. As an example of a high symmetry line, we consider a vector $\vec{k} = k \cdot \vec{e}_x$ (with small k). The symmetry group $G_0(\vec{k})$ is here C_{4v}. Again, the eigenspaces of $\hat{H}_0$ are representation spaces of this group, see Table 14.2, and given by vectors $\vec{G}$ with the same values of $\vec{G}^2 + 2\vec{k} \cdot \vec{G}$. The reduction leads to

$$\begin{aligned} \Gamma_0 = \Gamma_1 &= A_1 \,, \\ \Gamma_2 = \Gamma_3 &= A_1 + B_1 + E \,, \\ \Gamma_4 &= A_1 + B_2 + E \,. \end{aligned}$$

In Fig. 14.3 we show the numerical results for $V(\vec{G}) = 0$ (red dashed lines) and the artificial values

$$\begin{aligned} V(\vec{G}) &= -0.1 \ \text{ for } \ \vec{G}^2 = 0 \,, \\ V(\vec{G}) &= 0.1 \ \text{ for } \ \vec{G}^2 = 1 \,, \\ V(\vec{G}) &= -0.1 \ \text{ for } \ \vec{G}^2 = 2 \,, \\ V(\vec{G}) &= 0.1 \ \text{ for } \ \vec{G}^2 = 3 \,, \\ V(\vec{G}) &= 0 \ \text{ otherwise,} \end{aligned} \tag{14.11}$$

of the potential (black lines) where we have set $1/(2m) = 1$ such that energies are dimensionless. Most readers will be familiar with comparable figures in one dimension, since these are contained in most introductory books on solid-state physics. For example, if you follow the red line (i.e. the case of free particles) between Γ and X, one immediately recognizes the difference between one and three dimensions. At the (dimensionless) energy 1 we find two ascending bands, which would not exist in one dimension. The reason for this additional band is that in (14.9) there also exist vectors $\vec{G}_0$ which are perpendicular to the line $\Gamma \to X$, creating bands that do not exist in one dimension.

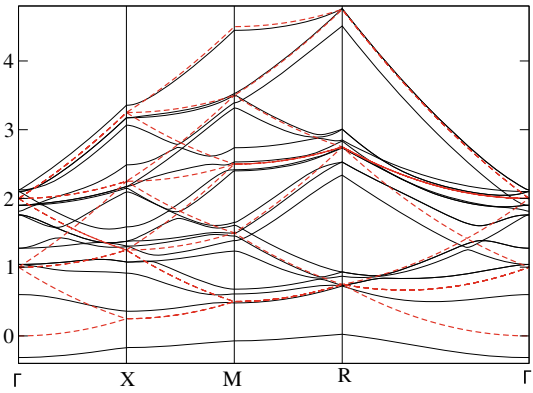

Fig. 14.3 The 19 lowest energy bands from a plane-wave expansion of electrons in a simple cubic lattice; red: $V(\vec{G}) = 0$; black: $V(\vec{G})$ given in (14.11)

14.5 Tight-Binding Models

14.5.1 Derivation of Tight-Binding Models

In a sense, we now go the opposite way of Sect. 14.4, starting from the atomic wave functions and merging them into a solid. As a first step, we assume that the *atomic* one-particle problem is solved, i.e. we start from the eigenstates $\eta_{i,\alpha}(\vec{r})$ of the local part of the Schrödinger equation,

$$\left(-\frac{\Delta_{\vec{r}}}{2m} + e^2\frac{Z_i}{|\vec{B}_i - \vec{r}|}\right)\eta_{i,\alpha}(\vec{r}) = \varepsilon_{i,\alpha}\eta_{i,\alpha}(\vec{r}) \ ,$$

with corresponding eigenvalues $\varepsilon_{i,\alpha}$. To simplify the notation, we introduce the index $\gamma \equiv (i, \alpha)$, which combines the lattice site index i and the orbital quantum number α. The corresponding orbital states $\eta_\gamma(\vec{r})$ are localized around their respective lattice site $\vec{B}_i$. However, these states may not necessarily be orthogonal to each other if the lattice sites are different. In general, we have:

$$\langle\eta_\gamma|\eta_{\gamma'}\rangle = \int d^3\vec{r}\ \eta^*_\gamma(\vec{r})\eta_{\gamma'}(\vec{r}) \equiv \delta_{\gamma,\gamma'} + S_{\gamma,\gamma'} \ , \tag{14.12}$$

where $S_{\gamma,\gamma'}$ are the elements of a finite *overlap-matrix* $\tilde{S}$. Following Löwdin [1], we introduce the matrix

$$\tilde{M} = (\tilde{1} + \tilde{S})^{-1/2} \approx \tilde{1} - \frac{1}{2}\tilde{S} + \frac{3}{8}\tilde{S}^2 - \cdots \ ,$$

which is well defined since $\tilde{S}$ is Hermitian and we assume that its eigenvalues s_i obey $|s_i| < 1$. The matrix $\tilde{M}$ defines a transformation to a new basis of states

$$\left|\bar{\eta}_\gamma\right\rangle = \sum_{\gamma'} M_{\gamma',\gamma} \left|\eta_{\gamma'}\right\rangle \ , \tag{14.13}$$

which are, by construction, orthogonal,

$$\langle\bar{\eta}_\gamma|\bar{\eta}_{\gamma'}\rangle = \sum_{\tilde{\gamma},\tilde{\gamma}'} M_{\gamma,\tilde{\gamma}} \underbrace{\langle\eta_{\tilde{\gamma}}|\eta_{\tilde{\gamma}'}\rangle}_{[\tilde{M}^{-1}\tilde{M}^{-1}]_{\tilde{\gamma},\tilde{\gamma}'}} M_{\tilde{\gamma}',\gamma'} = \delta_{\gamma,\gamma'} \ \surd \ .$$

The new states $\bar{\eta}_{i,\beta}(\vec{r}) = \langle\vec{r}|\bar{\eta}_{i,\beta}\rangle$ still retain a lattice site index i, but it is evident from (14.13) that they have a mixture of states $\eta_{i',\alpha}(\vec{r})$ at different sites $i' \neq i$. However, if the states $\eta_{i,\alpha}(\vec{r})$ are localized compared to the distances to neighboring sites, then the overlap-matrix elements $S_{(i,\alpha),(i',\alpha')}$ can be assumed to be small. Thus, the states $\bar{\eta}_{i,\alpha}(\vec{r})$ are also well localized around the site i, as the primary contribution in (14.13) comes from states at the same site.

With a proper basis of localized and orthogonal states, we can now diagonalize the local Hamilton matrix

$$H^i_{\beta,\beta'} \equiv \langle\bar{\eta}_{i,\beta}|\hat{H}|\bar{\eta}_{i,\beta'}\rangle$$

for each site i via some unitary transformation $T^i_{b,\beta}$,

$$\sum_{\beta,\beta'} T^i_{b,\beta} H^i_{\beta,\beta'} \left(T^i_{b',\beta'}\right)^* = \delta_{b,b'}\varepsilon_{i,b} \ .$$

The resulting eigenstates

$$\phi_{i,b}(\vec{r}) = \sum_{\beta} T^i_{b,\beta}\bar{\eta}_{i,\beta}(\vec{r}) \tag{14.14}$$

of $H^i_{\beta,\beta'}$ now have the proper site symmetry, i.e. they are classified by representations of the point-symmetry group of each site i. The advantage of our approach is that the orbitals have this property even when the crystal has a basis of more than one atom per Bravais lattice site. According to the author's impression, this is not the case with the derivations of tight-binding models found in most textbooks on solid-state physics.

With the orbital basis (14.14), the one-particle Hamiltonian $\hat{H}$ in first or second quantization has the *tight-binding* form

$$\hat{H}_0 = \sum_{i,j}\sum_{b,b'} t^{b,b'}_{i,j} |i,b\rangle\langle j,b'| = \sum_{i,j}\sum_{b,b'} t^{b,b'}_{i,j} \hat{c}^\dagger_{i,b}\hat{c}_{j,b'} \ .$$

The *hopping' parameters* $t_{i,j}^{b,b'}$ (also denoted as *tight-binding parameters*) are given as

$$t_{i,j}^{b,b'} \equiv \int \mathrm{d}^3 r \phi_{i,b}^*(\vec{r}) \hat{H} \phi_{j,b'}(\vec{r}) \ , \tag{14.15}$$

where the local parameters $t_{i,i}^{\sigma,\sigma'}$ are diagonal by construction,

$$t_{i,i}^{\sigma,\sigma'} = \delta_{\sigma,\sigma'} \varepsilon_{i,\sigma} \ .$$

14.5.2 The Slater Koster Parameters

Finally, we want to turn to the question how the hopping parameters (14.15) can be determined approximately. According to this equation we should, in principle, evaluate the following integral,

$$t_{i,j}^{b,b'} \equiv - \int \mathrm{d}^3 r \phi_b^*(\vec{r} - \vec{B}_i) \left(\frac{\Delta_{\vec{r}}}{2m} + \sum_l \frac{e^2}{|\vec{r} - \vec{B}_l|} \right) \phi_{b'}(\vec{r} - \vec{B}_j) \ ,$$

where the wave functions are the same as in (14.15). An idea going back to Slater and Koster (SK) [2] is to take into account only the two terms $l = i$ and $l = j$ in the sum over l, i.e. to approximate the hopping parameters as

$$\begin{aligned} t_{i,j}^{b,b'} &\equiv - \int \mathrm{d}^3 r \phi_b^*(\vec{r} - \vec{B}_i) \left(\frac{\Delta_{\vec{r}}}{2m} + \frac{e^2}{|\vec{r} - \vec{B}_i|} + \frac{e^2}{|\vec{r} - \vec{B}_j|} \right) \phi_{b'}(\vec{r} - \vec{B}_j) \\ &\equiv E(\phi_{i,b}; \phi_{j,b'}) \ . \end{aligned} \tag{14.16}$$

The obvious way at first glance, would be to determine the wave functions $\phi_b(\vec{r} - \vec{B}_i)$ and then calculate the integrals (14.16) with them. However, this is not a sensible approach, because we have completely neglected the electronic interactions in our considerations so far. Even in systems where these are indeed small, they will still modify band structures quantitatively and must be considered at least at the level of effective one-particle theories, such as the density functional theory. The question then often arises (for example, in calculations with more demanding correlation methods) how a calculated band structure can be approximated near the Fermi energy using as few independent tight-binding parameters as possible (*tight-binding fit*). With (14.16) one is dealing with the problem of a diatomic molecule. As an example, we illustrate in Fig. 14.4 the hopping processes between an s orbital and two examples of p_y, p_z orbitals which have the same distance from the s orbital. We want to calculate the hopping parameters between the orbitals, which are defined with respect to the cubic axes, for example, the orbitals (8.8)–(8.9) or the unprimed orbitals $p_y \sim y$, $p_z \sim z$ in Fig. 14.4. It is more convenient, however, to analyze the primed orbitals group-theoretically, where the z-axis is defined along the vector

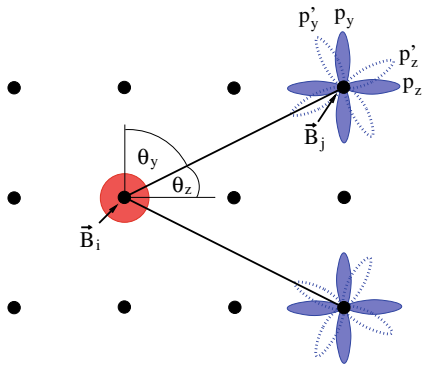

Fig. 14.4 Determination of the Slater Koster parameters

$$\vec{B} \equiv \vec{B}_j - \vec{B}_i$$

For the primed orbitals, the analysis is simplest using the tesseral wave functions already introduced in Chap. 8,

$$\bar{Y}'_{l,m} \equiv \begin{cases} \frac{1}{2}(Y'_{l,m} + Y'_{l,-m}) \sim \cos(m \cdot \varphi) & (m \geq 0) \\ \frac{1}{2\mathrm{i}}(Y'_{l,|m|} - Y'_{l,-|m|}) \sim \sin(m \cdot \varphi) & (m < 0) \end{cases} .$$

Due to the integral over φ in (14.16), it is evident that

$$E(\bar{Y}'_{l,m}; \bar{Y}'_{l',m'}) \sim \delta_{m,m'} .$$

Since

$$\int_0^{2\pi} \mathrm{d}\varphi \sin(m \cdot \varphi)^2 = \int_0^{2\pi} \mathrm{d}\varphi \cos(m \cdot \varphi)^2$$

this further implies that

$$E(\bar{Y}'_{l,m}; \bar{Y}'_{l',m}) = E(\bar{Y}'_{l,-m}; \bar{Y}'_{l,-m}) .$$

Thus for $l, l' \leq 2$ there are three types of integrals (14.16), $m = 0, 1, 2$ ($m \leq \min(l, l')$) which have been denoted as ρ, π, δ by SK. With the usual designation of the orbitals as s, p, d we obtain the SK symbols

$$(ss\rho) \equiv E(\bar{Y}'_{0,0}; \bar{Y}'_{0,0}), \ (pd\pi) \equiv E(\bar{Y}'_{1,1}; \bar{Y}'_{2,1}), \ (dd\delta) \equiv E(\bar{Y}'_{2,2}; \bar{Y}'_{2,2}) \ \ldots$$

for the integrals.

We have now clarified which independent hopping parameters exist between the unprimed orbitals. Without giving a detailed explanation, SK come to the conclusion that the relationship between the unprimed and canceled orbitals can be expressed by the direction cosines θ_i [3],

$$(\cos\theta_x, \cos\theta_y, \cos\theta_z)^T \equiv \frac{\vec{B}}{|\vec{B}|} .$$

This results in, e.g. the following relations (all others can be found in table I of SK)

$$E(x, yz) = \sqrt{3}lmn(pd\sigma) - 2lmn(pd\pi) ,$$
$$E(xy, xy) = 3l^2m^2(dd\sigma) + (l^2 + m^2 - 4l^2m^2)(dd\pi) + (n^2 + l^2m^2)(dd\delta) .$$

With the knowledge of the relationships between the unoccupied and occupied orbitals, the Hamilton matrices in $\vec{k}$-space can be determined by means of a Fourier transformation. For example, in a cubic environment (with lattice constant $a = 1$), the following two matrix elements (with hopping contributions up to the third nearest neighbor) can be derived,

$$H_{s,xy} = -2\sqrt{3}(sd\sigma)_2 \sin k_x \sin k_y - \frac{8}{\sqrt{3}}(sd\sigma)_3 \sin k_x \sin k_y \cos k_z$$
$$H_{xy,xz} = 2[-(dd\pi)_2 + (dd\delta)_2] \sin k_y \sin k_z + \left[-\frac{8}{3}(dd\sigma)_3 + \frac{8}{9}(dd\pi)_3 + \frac{16}{9}(dd\delta)_3\right] \cos k_x \sin k_y \sin k_z$$

All other matrix elements are given in Table III of SK.

Exercises

1. Like in Sect. 14.4, determine the first 5 eigenspaces of $\hat{H}_0$ (see (14.8)) for the vectors $\vec{k} = k(\vec{e}_x + \vec{e}_y + \vec{e}_z)$ (for small positive k). How do these split up in leading order when the potential $V(\vec{G})$ is switched on?
2. We consider a tight-binding model described by the Hamiltonian

$$\hat{H} = \sum_{i \neq j} \sum_{b,b'} t_{i,j}^{b,b'} |i, b\rangle\langle i, b'|$$

in which at each (simple cubic) lattice site there are two degenerate e_g orbitals ($b, b' = 1, 2$). If we assume that $t_{i,j}^{b,b'}$ is non-zero only between next neighbors, then after a transformation into the wave vector space we obtain (see Sect. 14.5.2)

$$\hat{H} = \sum_{\vec{k}} \sum_{b,b'} \epsilon_{b,b'}(\vec{k}) |\vec{k}, b\rangle\langle\vec{k}, b'| = \sum_{\vec{k}} \hat{H}_{\vec{k}},$$

where

$$\epsilon_{1,1}(\vec{k}) = t_\sigma(\cos k_x + \cos k_y + 4\cos k_z) + 3t_\delta(\cos k_x + \cos k_y)$$
$$\epsilon_{2,2}(\vec{k}) = 3t_\sigma(\cos k_x + \cos k_y) + t_\delta(\cos k_x + \cos k_y + 4\cos k_z)$$
$$\epsilon_{1,2}(\vec{k}) = \sqrt{3}[t_\delta - t_\sigma](\cos k_x - \cos k_y)$$

and t_σ, t_δ are parameters (not fixed by symmetry).

(a) Determine the band structure by a diagonalization of $\hat{H}_{\vec{k}}$.
(b) Verify the degeneracy of all stars of $\vec{k}$.
(c) Along which of the high symmetry lines $\Gamma \to X$, $\Gamma \to M$, $\Gamma \to R$ is the spectrum of $\hat{H}_{\vec{k}}$ degenerate? Explain this degeneracy with group theoretical arguments.

References

1. P.-O. Löwdin. J. Chem. Phys., 18:365, 1950.
2. J. C. Slater and G. F. Koster. Phys. Rev. 94, 1498
3. A clean derivation that can also be used beyond the *d* orbitals, can be found in R. R. Sharma, Phys. Rev. **B**, 19, 1979.

Appendix A
The Schoenflies and the International Notation

There are two established ways of naming point groups, the *Schoenflies* and the *international notation*. The Schoenflies notation is used more often if one is only interested in the point groups. In contrast, the international one is mainly to denote the rotational part of space groups. We will give a brief introduction to both notations in this appendix.

A.1 The Schoenflies Notation

In the Schoenflies notation, the proper point groups are named in the same way as they were introduced in Sect. 3.2. Most of the names of the improper point groups are derived from those of the proper ones by specifying which additional improper symmetry operations exist in the group. Historically, the notation of the groups argued with the existing mirror planes and did not use the inversion. We go a slightly different way here to motivate the notation:

(i) The groups C_i, C_{2h}, S_6, C_{4h}, D_{2h}, D_{3d}, C_{6h}, D_{4h}, D_{6h}, T_h, O_h:
These groups are constructed by adding the inversion I to the respective 11 proper point groups G_0 in (3.7), $G = G_0 \times (E, I)$. For the proper point groups $G_0 = \{C_1, C_6\}$ the notations C_i, S_6 are used instead of C_{1h}, C_{6h}. Remember that all these groups also contain some mirror planes, since these correspond to a product of a two-fold rotation and the inversion (see Sect. 3.1).

(ii) The groups C_s, C_{3h}, D_{3h}:
These groups are constructed by adding a mirror plane σ_h perpendicular to the main symmetry axis δ_n to the respective proper point groups C_1, C_3, D_3. In case of D_3 the two-fold axes, perpendicular to δ_n, must obviously lie in σ_h.

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(iii) The groups C_{nv} ($n = 2, 3, 4, 6$):
These groups are constructed by adding n mirror planes to C_n ($n = 2, 3, 4, 6$) that all contain the axis of symmetry and have the same angle relative to each other.

(iv) The groups S_4, D_{2d}, T_d ($n = 2, 3, 4, 6$):
These groups are constructed by replacing the two-fold symmetry axis in C_2, D_2, T by a four-fold *rotary inversion* axis $\sigma_4 \equiv I \cdot \delta_4$. Since $(\sigma_4)^2 = \delta_2$, the corresponding proper groups are subgroups in all three cases. Note that T_d is the symmetry group of a tetrahedron.

A.2 The International Notation

The international notation considers the three possible types of rotational symmetry axes:

(i) proper n-fold rotation axes δ_n are denoted as $n = 2, 3, 4, 6$.

(ii) n-fold rotary inversion axes $I \cdot \delta_n$ are denoted as $\bar{n}$ with $n = 1, 2, 3, 4, 6$. Then, an axis $\bar{n}$ contains the symmetry elements shown in Table A.1. In that table we use the common abbreviations

$$\sigma_2 \equiv \sigma \equiv I \cdot \delta_2 \ , \ \sigma_6 \equiv I \cdot \delta_3 \ , \ \sigma_4 \equiv I \cdot \delta_4 \ , \ \sigma_3 \equiv I \cdot \delta_6 \ .$$

Since a rotary inversion axes $\bar{2}$ is equivalent to a mirror plane, one often writes 'm' instead of '$\bar{2}$' .

(iii) If n is odd, $\bar{n}$ necessarily contains I, because

$$(I \cdot \delta_n)^n = \underbrace{I^n}_{I} \cdot \underbrace{\delta_n^n}_{E} = I$$

Therefore, the definition of the third kind of axes of rotation only makes sense for even n:

$$\frac{n}{m} \equiv \bar{n} \cup I$$

Table A.1 Elements of a rotary inversion axes $\bar{n}$

$\bar{n}$	Elements	Order $g(\bar{n})$
$\bar{1}$	$E\ I$	2
$\bar{2}$	$E\ \sigma$	2
$\bar{3}$	$E\ \sigma_6\ \delta_3^{-1}\ I\ \delta_3\ \sigma_6^{-1}$	6
$\bar{4}$	$E\ \sigma_4\ \delta_2\ \sigma_4^{-1}$	4
$\bar{6}$	$E\ \sigma_3\ \delta_3\ \sigma\ \delta_3^{-1}\ \delta_3^{-1}$	6

Table A.2 Elements of a rotary inversion axes $\frac{n}{m}$ for even n

$\bar{n}$	Elements	Order $g\left(\frac{n}{m}\right)$
$\frac{2}{m}$	$E\ \sigma\ I\ \delta_2$	4
$\frac{4}{m}$	$E\ \sigma_4\ \delta_2\ \sigma_4^{-1}\ I\ \delta_4\ \sigma\ \delta_4^{-1}$	8
$\frac{6}{m}$	$E\ \sigma_3\ \delta_3\ \sigma\ \delta_3^{-1}\ \delta_3^{-1}\ I\ \delta_6\ \sigma_6\ \delta_2\ \sigma_6^{-1}\ \delta_6^{-1}$	12

The elements of an axis $\frac{n}{m}$ are shown in Table A.2.

We can now formulate the rules of the international notation.

(i) Identify all occurring axes of the form $n, \bar{n}, \frac{n}{m}$.
(ii) Equivalent axes are represented by a common symbol. Equivalence here means that the axes can be mapped onto one another by a symmetry operation. An exception is the group $D_2 = 222$, where all three axes occur since otherwise the group would not be distinguishable from $C_2 = 2$.
(iii) The symbol of the point group is then simply the list of the occurring symbols $n, \bar{n}, \frac{n}{m}$. sorted according to the order of the axes. Again there are expectations, like $T = 23$, which has to be distinguished from $D_3 = 32$.

Appendix B
Solutions to the Exercises

Chapter 1

1. It is sufficient to show that

$$\langle \vec{r}|\hat{T}_{\tilde{D}^{-1}} \cdot \hat{T}_{\tilde{D}}|\vec{r}'\rangle = \delta(\vec{r} - \vec{r}') \ , \tag{B.1}$$

for all basis states $|\vec{r}\rangle$, $|\vec{r}'\rangle$. When we insert a one-operator $\hat{1}$ built with these states, we find

$$\begin{aligned}\langle \vec{r}|\hat{T}_{\tilde{D}^{-1}} \cdot \hat{T}_{\tilde{D}}|\vec{r}'\rangle &= \int \mathrm{d}^3 r'' \langle \vec{r}|\hat{T}_{\tilde{D}^{-1}}|\vec{r}''\rangle\langle \vec{r}''|\hat{T}_{\tilde{D}}|\vec{r}'\rangle \\ &= \int \mathrm{d}^3 r'' \langle \tilde{D}^{-1} \cdot \vec{r}|\vec{r}''\rangle\langle \tilde{D} \cdot \vec{r}''|\vec{r}'\rangle \ . \end{aligned} \tag{B.2}$$

Since

$$\langle \tilde{D}^{-1} \cdot \vec{r}|\vec{r}''\rangle = \langle \vec{r}|\tilde{D} \cdot \vec{r}''\rangle = \delta(\vec{r} - \tilde{D} \cdot \vec{r}'')$$

and

$$\langle \tilde{D} \cdot \vec{r}''|\vec{r}'\rangle = \delta(\vec{r}' - \tilde{D} \cdot \vec{r}'')$$

Equation (B.1) follows from (B.2).

2. (a) With the definition of the momentum operator $\hat{\vec{p}} = -\frac{\mathrm{i}}{\hbar}\vec{\nabla}$, it follows

$$\hat{T}_{\vec{a}} \cdot \Psi(\vec{r}) = \sum_{j=1}^{\infty} \frac{1}{j!}(\vec{a} \cdot \vec{\nabla})^j \Psi(\vec{r})$$

which is just the Taylor-expansion of $\Psi(\vec{r} + \vec{a})$.

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(b) In spherical coordinates it is $\hat{L}_z = \frac{\hbar}{\mathrm{i}} \frac{\partial}{\partial \varphi}$. Thus, we find

$$\hat{T}_\alpha \cdot \Psi(r, \theta, \varphi) = \sum_{j=1}^{\infty} \frac{1}{j!} \left(\frac{\partial}{\partial \varphi} \right)^j \Psi(r, \theta, \varphi) = \Psi(r, \theta, \varphi + \alpha) \quad . \surd$$

Since the z-direction is not distinguished from all other, for any other direction $\vec{e}$ ($|\vec{e}| = 1$) of the rotation it must be

$$\hat{T}_{\alpha, \vec{e}} = \exp\left(\frac{\mathrm{i}}{\hbar} \alpha \left(\vec{e} \cdot \hat{\vec{L}} \right) \right) = \exp\left(\vec{\alpha} \cdot \hat{\vec{L}} \right) \equiv \hat{T}_{\vec{\alpha}}$$

with a vector $\vec{\alpha} \equiv \alpha \cdot \vec{e}$.

3. We follow the idea for a proof proposed in the exercise:

(i) Using well-known properties of determinants we can derive:

$$\begin{aligned} |\tilde{1} - \tilde{D}| &= \underbrace{|\tilde{D}|}_{=1} |\tilde{1} - \tilde{D}| = |\tilde{D}^T||\tilde{1} - \tilde{D}| = |\tilde{D}^T - \tilde{1}| = |\tilde{D} - \tilde{1}| \\ &= -|\tilde{1} - \tilde{D}| \; . \end{aligned}$$

Therefore, it is $|\tilde{1} - \tilde{D}| = 0$, which means that $\lambda = 1$ is an eigenvalue of $\tilde{D}$.

(ii) In a complex vector space, $\tilde{D}$ has 3 complex eigenvalues λ_i and there is a unitary matrix $\tilde{U}$ such that

$$\tilde{U} \cdot \tilde{D} \cdot \tilde{U}^\dagger = \tilde{D}^{\mathrm{d}} \equiv \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix} \; .$$

With

$$\tilde{D}^{\mathrm{d}} \cdot (\tilde{D}^{\mathrm{d}})^\dagger = \tilde{U} \cdot \tilde{D} \cdot \tilde{U}^\dagger \cdot \tilde{U} \cdot \tilde{D}^\dagger \cdot \tilde{U}^\dagger = \tilde{U} \cdot \tilde{D} \cdot \tilde{D}^\dagger \cdot \tilde{U}^\dagger = \tilde{U} \cdot \tilde{U}^\dagger = \tilde{1} \; ,$$

we can conclude that

$$\lambda_i^2 = 1 \quad \Rightarrow \quad \lambda_i = e^{\mathrm{i}\varphi_i} \; ,$$

with $\varphi_i \in \mathbb{R}$. Since one of these eigenvalues is 1 (e.g. $\varphi_3 = 0$) and $|\tilde{D}| = |\tilde{D}^{\mathrm{d}}| = 1$, it must be $\varphi_1 = -\varphi_2 \equiv \varphi$.

(iii) For $\varphi \neq 0$, the three eigenvectors $\vec{v}_i$ are orthogonal, because[1]

$$\vec{v}_i^\dagger \cdot \tilde{D} \cdot \vec{v}_j = e^{\mathrm{i}\varphi_i} \vec{v}_i^\dagger \cdot \vec{v}_j = e^{\mathrm{i}\varphi_j} \vec{v}_i^\dagger \cdot \vec{v}_j \quad \Rightarrow \quad \vec{v}_i^\dagger \cdot \vec{v}_j = \delta_{i,j} \; .$$

[1] Remember that $\hat{D}^T \vec{v}_i = e^{-\mathrm{i}\varphi} \vec{v}_i$.

If we split the two vectors $\vec{v}_1, \vec{v}_2$ into their real and imaginary parts

$$\vec{v}_{1,2} = \frac{1}{\sqrt{2}}(\vec{v}_\mathrm{R} \pm \mathrm{i}\vec{v}_\mathrm{I}) \ ,$$

the real vectors $\vec{v}_\mathrm{R}, \vec{v}_\mathrm{I}$ are also orthogonal. We can then use the inverse

$$\vec{v}_\mathrm{R} = \frac{1}{\sqrt{2}}(\vec{v}_1 + \vec{v}_2) \ ,$$
$$\vec{v}_\mathrm{I} = \frac{1}{\mathrm{i}\sqrt{2}}(\vec{v}_1 - \vec{v}_2)$$

to calculate the 4 matrix elements $\vec{v}_{\mathrm{R,I}} \cdot \tilde{D} \cdot \vec{v}_{\mathrm{R,I}}$. This results in the following matrix in the basis of the (real) vectors $\vec{v}_\mathrm{R}, \vec{v}_\mathrm{I}, \vec{v}_3$

$$\tilde{D}' = \begin{pmatrix} \cos(\varphi) & \sin(\varphi) & 0 \\ -\sin(\varphi) & \cos(\varphi) & 0 \\ 0 & 0 & 1 \end{pmatrix} \ . \surd$$

4. (a) The symmetry transformations are

   (i) Three axes of rotation $\vec{e}_x, \vec{e}_y, \vec{e}_z$ with rotation angles of π.
   (ii) The inversion at the origin.
   (iii) Three mirror planes, in each of which there are two axes of rotation.

   We refer to this symmetry group in Chap. 3 as D_{2h}.

   (b) The symmetry transformations are

   (i) An axis of rotation $\vec{e}_z$ with a rotation angle of π.
   (ii) The inversion at the origin.
   (iii) The mirror plane perpendicular to the axis of rotation.
   (iv) The two rotation axes $y = x$ and $y = -x$ with a rotation angle of π. They induce the transformation

   $$x \to y \text{ and } y \to x \ ,$$

   and

   $$x \to -y \text{ and } y \to -x \ .$$

   (v) Two mirror planes parallel to $\vec{e}_z$ in which the rotation axes (iv) lie.

   A comparison with (a) shows that this is exactly the same group D_{2h}.

Chapter 2

1. (a) Suppose that there are two elements $E_1 \neq E_2$ with $E_1 \cdot a = a$ and $E_2 \cdot a = a$ for all $a \in G$. Multiplying

$$E_1 \cdot a = a$$

from the right with a^{-1} yields $E_1 = E_2$. $\surd$

(b) The proof is the same as in (a) replacing E_i by a_i^{-1}.

(c) Let us assume that for every $a \in G$ there is a left inverse element a_{L}^{-1} with

$$a_{\mathrm{L}}^{-1} \cdot a = E \ .$$

If we multiply this equation from the left with a it follows

$$a \cdot a_{\mathrm{L}}^{-1} \cdot a = a \quad \Rightarrow \quad a \cdot a_{\mathrm{L}}^{-1} = E \quad \Rightarrow \quad a_{\mathrm{R}}^{-1} = a_{\mathrm{L}}^{-1} \ . \surd$$

2. With Table 2.5 we find for the class multiplications ($\mathcal{C}_1 \cdot \mathcal{C}_i = \mathcal{C}_i$ obviously holds)

$$\begin{aligned}
\mathcal{C}_2 \cdot \mathcal{C}_3 &= \{\delta_3 \cdot \delta_{21}, \delta_3 \cdot \delta_{22}, \delta_3 \cdot \delta_{23}, \delta_3^2 \cdot \delta_{21}, \delta_3^2 \cdot \delta_{22}, \delta_3^2 \cdot \delta_{23}\} \\
&= \{\delta_{23}, \delta_{21}, \delta_{22}, \delta_{22}, \delta_{23}, \delta_{21}\} = 2\mathcal{C}_3 \ , \surd \\
\mathcal{C}_3 \cdot \mathcal{C}_3 &= \{\delta_{21} \cdot \delta_{21}, \delta_{21} \cdot \delta_{22}, \delta_{21} \cdot \delta_{23}, \delta_{22} \cdot \delta_{21}, \delta_{22} \cdot \delta_{22}, \delta_{22} \cdot \delta_{23}, \\
&\quad \delta_{23} \cdot \delta_{21}, \delta_{23} \cdot \delta_{22}, \delta_{23} \cdot \delta_{23}\} \\
&= \{E, \delta_3, \delta_3^2, \delta_3^2, E, \delta_3, \delta_3, \delta_3^2, E\} = 3\mathcal{C}_1 \cdot \mathcal{C}_2 \ . \surd
\end{aligned}$$

3. If $f(a) = a^{-1}$ satisfies (2.15), we have

$$\underbrace{(a^{-1} \cdot b^{-1})^{-1}}_{=b \cdot a} = \underbrace{(a^{-1})^{-1} \cdot (b^{-1})^{-1}}_{a \cdot b} \ . \surd$$

4. (a) The elements of G are E, the three 4-fold rotations δ_4, δ_4^2, δ_4^3 around the symmetry axis of the molecule and the 4 mirror planes $\sigma_1, \ldots, \sigma_4$ shown in Fig. B.1. The inverse elements are

$$\begin{aligned}
(\delta_4)^{-1} &= \delta_4^3 \ , \\
(\delta_4^2)^{-1} &= \delta_4^2 \ , \\
(\delta_4^3)^{-1} &= \delta_4 \ , \\
(\sigma_i)^{-1} &= \sigma_i \quad (i = 1, \ldots, 4) \ .
\end{aligned}$$

As illustrated in the example of the group D_3 in Sect. 2.2.3, each group element corresponds to an arrangement of the vertices of the molecule (here A, B, C, D) after the group transformation. These are for the 8 group elements

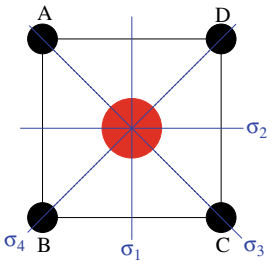

Fig. B.1 Mirror planes in the molecule of Exercise 2

$$
\begin{aligned}
(A, B, C, D) &\xrightarrow{E} (A, B, C, D)\\
&\xrightarrow{\delta_4} (D, A, B, C)\\
&\xrightarrow{\delta_4^2} (C, D, A, B)\\
&\xrightarrow{\delta_4^3} (B, C, D, A)\\
&\xrightarrow{\sigma_1} (B, A, C, D)\\
&\xrightarrow{\sigma_2} (A, B, D, C)\\
&\xrightarrow{\sigma_3} (C, D, B, A)\\
&\xrightarrow{\sigma_4} (D, C, A, B)\ .
\end{aligned}
$$

Herewith we can determine which group elements result from the multiplication of two elements. The results are shown in Table B.1.

(b) The sub-groups are

$$\{E\}, \{E, \delta_4^2\}, \{E, \delta_4, \delta_4^2, \delta_4^3\}, \{E, \sigma_i\}, \{E, \delta_4^2, \sigma_1, \sigma_2\}, \{E, \delta_4^2, \sigma_3, \sigma_4\}\ .$$

(c) If two elements a_1, a_2 are in the same class the corresponding orthogonal matrices $\tilde{D}_1$, $\tilde{D}_2$ must obey

Table B.1 Multiplication table for the symmetry group of the molecule in Fig. B.1

	E	δ_4	δ_4^2	δ_4^3	σ_1	σ_2	σ_3	σ_4
E	E	δ_4	δ_4^2	δ_4^3	σ_1	σ_2	σ_3	σ_4
δ_4	δ_4	δ_4^2	δ_4^3	E	σ_3	σ_4	σ_2	σ_1
δ_4^2	δ_4^2	δ_4^3	E	δ_4	σ_2	σ_1	σ_4	σ_3
δ_4^3	δ_4^3	E	δ_4	δ_4^2	σ_4	σ_3	σ_1	σ_2
σ_1	σ_1	σ_4	σ_2	σ_3	E	δ_4^2	δ_4^3	δ_4
σ_2	σ_2	σ_3	σ_1	σ_4	δ_4^2	E	δ_4	δ_4^3
σ_3	σ_3	σ_1	σ_4	σ_2	δ_4	δ_4^3	E	δ_4^2
σ_4	σ_4	σ_2	σ_3	σ_1	δ_4^3	δ_4	δ_4^2	E

Table B.2 Multiplication table of the matrix group (2.16)

	D_1	D_2	D_3	D_4	D_5	D_6
D_1	D_1	D_2	D_3	D_4	D_5	D_6
D_2	D_2	D_3	D_1	D_5	D_6	D_4
D_3	D_3	D_1	D_2	D_6	D_4	D_5
D_4	D_4	D_6	D_5	D_1	D_3	D_2
D_5	D_5	D_4	D_6	D_2	D_1	D_3
D_6	D_6	D_5	D_4	D_3	D_2	D_1

$$\tilde{D}_1 = \tilde{D}^{-1} \cdot \tilde{D}_2 \cdot \tilde{D}$$

with some other matrix $\tilde{D}$ of the group. Hence, $|\tilde{D}_1| = |\tilde{D}_2|$ from which we can conclude that δ_4^i and σ_i cannot be in the same class.[2] Since

$$\sigma_1^{-1} \cdot \delta_4 \cdot \sigma_1 = \delta_4^3 \ ,$$

δ_4 and δ_4^3 are in the same class. There is no such relationship for δ_4^2 which therefore is a class on its own. With

$$\delta_4^{-1} \cdot \sigma_4 \cdot \delta_4 = \delta_4^3 \cdot \sigma_4 \cdot \delta_4 = \sigma_3$$

we find that σ_3 and σ_4 are in the same class. The same follows for σ_1 and σ_2. We give two examples of class multiplications

$$\{\delta_4, \delta_4^3\} \cdot \{\delta_4^2\} = \{\delta_4, \delta_4^3\} \ ,$$
$$\{\sigma_1, \sigma_2\} \cdot \{\delta_4, \delta_4^3\} = 2 \cdot \{\sigma_3, \sigma_4\} \ .$$

(d) According to Sect. 2.3.5 a sub-group is normal if it consists of a set of complete classes. This is the case for all sub-groups in (b) except $\{E, \sigma_i\}$.

5. The multiplication table is given in Table B.2. According to that table, D_1 is obviously the identity element and each element has an inverse. The associative law is also fulfilled for matrix multiplication. Since the group is not Abelian, it must be isomorphic to the group D_3.
6. We need to show that

$$\sum_{l \in C_i, m \in C_j} a_l \cdot b_m = \sum_{l \in C_i, m \in C_j} b_m \cdot a_l \ .$$

[2] We could also use the fact here that the traces of $\tilde{D}_1$ and $\tilde{D}_2$ must be the same. These traces will be calculated in Chap. 3.

With the rearrangement theorem (2.6) for classes we find

$$\sum_{l,m} a_l \cdot b_m = \sum_m \left[\sum_l a_l \right] \cdot b_m \overset{(2.6)}{=} \sum_m \left[\sum_l b_m \cdot a_l \cdot b_m^{-1} \right] \cdot b_m = \sum_{m,l} b_m \cdot a_l \; . \; \surd$$

7. (a) Let a be any element of order n. Then, the subset

$$a, a^2, \ldots, a^n = E$$

of the group forms a sub-group of order n. With the considerations on cosets in Sect. 2.3.4 the assertion follows.

(b) Let n be the order of an element a and

$$b = x^{-1} \cdot a \cdot x$$

be an element in the same class. Then

$$b^n = (x^{-1} \cdot a \cdot x)^n = x^{-1} \cdot a^n \cdot x = x^{-1} \cdot E \cdot x = E \; . \; \surd$$

8. Since the multiplication properties of the identity element are the same for all groups, we only have to look at the other three group elements a_2, a_3, a_4. Each of these three elements must have an inverse. However, there are only 2 possibilities for this

(i) All elements are their own inverse. This group is isomorphic to D_2.
(ii) Two of the elements are mutual inverses. Then, the remaining element must be its own inverse. This group is isomorphic to C_4.

9. Take any element a of the group (of order g) and form the series of group elements $a_i = a^i, i = 1, 2, \ldots$. Then if $a_n = E$ for a $n < g$, the set of elements $a_1, \ldots, a_n$ would form a non-trivial sub-group. Hence, it can be $a_n = E$ only for $n = g$ and thus the group is cyclic, where (in this case) each element can be used as a generating element.$\surd$
Conversely, let us assume that the group is not cyclic. Here, too, $a^i \neq E$ must apply to every element a of the group if $i < g$ and $a^g = E$. However, if l is a divisor of the group order g, the elements $a^{g/l}, a^{2g/l}, \ldots, a^{lg/l} = E$ form a non-trivial sub-group contrary to the assumption.$\surd$
10. Axiom (1) is satisfied by definition. Therefore we only have to check whether Axioms (2)–(4) can be fulfilled.

(a) (2) The associative law is obviously fulfilled, because no matter in which order you carry out the multiplication, the largest element always comes out.

(3) The smallest natural number $a = 1$ is the identity element.
(4) An inverse element cannot be defined, since for all $\{a, b\} \neq E$

$$a \cdot b \neq E \ .$$

(b) (2) The associative law is obviously fulfilled.
(3) The identity element is $a = -1$.
(4) Let us assume that there is an inverse a^{-1} of a, which then has to satisfy

$$a^{-1} + a + 1 = -1 \quad \Rightarrow \quad a^{-1} = -a - 2 \ ,$$

and is well defined. Therefore, S is a group.

(c) (2) It is

$$(a \cdot b) \cdot c = a \cdot b \cdot c + \underline{b \cdot a \cdot c} + \underline{c \cdot a \cdot b} + c \cdot b \cdot a \ ,$$
$$a \cdot (b \cdot c) = a \cdot b \cdot c + \underline{a \cdot c \cdot b} + \underline{b \cdot c \cdot a} + c \cdot b \cdot a \ .$$

The terms underlined appear only in one of the equations. Hence, the associative law is not satisfied.
(3) The identity element is $E = \frac{1}{2}\tilde{1}$.
(4) It must then be

$$E^{-1} = E \quad \Rightarrow \quad \frac{1}{4}\tilde{1} = \frac{1}{2}\tilde{1} \ .$$

which is not the case. Hence, the axiom cannot be satisfied.

11. Probably the easiest way to solve this problem using a computer is to represent the transformations as 3-dimensional matrices,

$$\tilde{P}_1 = \begin{pmatrix} 1\,0\,0 \\ 0\,1\,0 \\ 0\,0\,1 \end{pmatrix} \ , \quad \tilde{P}_2 = \begin{pmatrix} 0\,0\,1 \\ 1\,0\,0 \\ 0\,1\,0 \end{pmatrix} \ , \quad \tilde{P}_3 = \begin{pmatrix} 0\,1\,0 \\ 0\,0\,1 \\ 1\,0\,0 \end{pmatrix} \ ,$$
$$\tilde{P}_4 = \begin{pmatrix} 0\,1\,0 \\ 1\,0\,0 \\ 0\,0\,1 \end{pmatrix} \ , \quad \tilde{P}_5 = \begin{pmatrix} 0\,0\,1 \\ 0\,1\,0 \\ 1\,0\,0 \end{pmatrix} \ , \quad \tilde{P}_6 = \begin{pmatrix} 1\,0\,0 \\ 0\,0\,1 \\ 0\,1\,0 \end{pmatrix} \ .$$

This leads to the multiplication Table B.3. This multiplication table is identical to that in Table B.2, i.e. the group is isomorphic to D_3.

Table B.3 Multiplication table of the permutation group

	P_1	P_2	P_3	P_4	P_5	P_6
P_1	P_1	P_2	P_3	P_4	P_5	P_6
P_2	P_2	P_3	P_1	P_5	P_6	P_4
P_3	P_3	P_1	P_2	P_6	P_4	P_5
P_4	P_4	P_6	P_5	P_1	P_3	P_2
P_5	P_5	P_4	P_6	P_2	P_1	P_3
P_6	P_6	P_5	P_4	P_3	P_2	P_1

Chapter 3

1. The class division of the groups D_n, claimed in Sect. 3.2, for $n = 3$ has the form

$$D_3 = \{E\} \cup \{\delta_3, \delta_3^2\} \cup \{\delta_{2,1}, \delta_{2,2}, \delta_{2,3}\} \ .$$

Since the traces (see (3.5)) of rotation matrices in a class must be identical, 3- and 2-fold rotations cannot be in the same class. Therefore, we only have to show that (using Table 2.5)

$$(\delta_{21})^{-1} \cdot \delta_3 \cdot \delta_{21} = \delta_{21} \cdot \underbrace{\delta_3 \cdot \delta_{21}}_{=\delta_{23}} = \delta_3^2 \quad \Rightarrow \quad \delta_3 \sim \delta_3^2 \ ,$$

$$(\delta_3)^{-1} \cdot \delta_{2,1} \cdot \delta_3 = \delta_3^2 \cdot \underbrace{\delta_{2,1} \cdot \delta_3}_{=\delta_{2,2}} = \delta_{2,3} \quad \Rightarrow \quad \delta_{2,1} \sim \delta_{2,3} \ ,$$

$$(\delta_3^2)^{-1} \cdot \delta_{2,1} \cdot \delta_3^2 = \delta_3 \cdot \underbrace{\delta_{2,1} \cdot \delta_3^2}_{=\delta_{2,3}} = \delta_{2,2} \quad \Rightarrow \quad \delta_{2,1} \sim \delta_{2,2} \ .$$

2. (a) The 2-fold rotation axis along the x-axis ($\delta_2^{\parallel}$) is easy to recognize. To identify the other two, it is helpful to imagine the atoms marked in black as being placed at the corners of a cuboid with two square faces (see Fig. B.2). The other two such axes ($\delta_{2,1}^{\perp}$, $\delta_{2,2}^{\perp}$) are shown in green in this figure. There are four other improper symmetry transformations. Two of these are easy

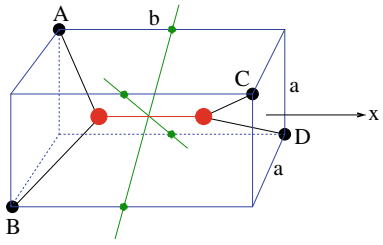

Fig. B.2 The molecule in Exercise 2

to recognize; the mirror plane σ_1 (σ_2) in which the positions A and B (C and D) are located. Moreover, the x-axis is not only a two-fold rotation axis, but also a four-fold rotation inversion axis ($\sigma_{4,1}$, $\sigma_{4,2} = \sigma_{4,1}^3$). The effect of all 8 group elements is given by the position of the four black atoms:

$$\begin{aligned}
(A, B, C, D) &\xrightarrow{E} (A, B, C, D)\\
&\xrightarrow{\delta_2^{\parallel}} (B, A, D, C)\\
&\xrightarrow{\delta_{2,1}^{\perp}} (D, C, B, A)\\
&\xrightarrow{\delta_{2,2}^{\perp}} (C, D, A, B)\\
&\xrightarrow{\rho_1} (B, A, C, D)\\
&\xrightarrow{\rho_2} (A, B, D, C)\\
&\xrightarrow{\sigma_{4,1}} (C, D, B, A)\\
&\xrightarrow{\sigma_{4,2}} (D, C, A, B)\ .
\end{aligned}$$

This leads to the multiplication Table B.4. Obviously, all group elements are their own inverses, except for $\sigma_{4,1}^{-1} = \sigma_{4,2}$, $\sigma_{4,2}^{-1} = \sigma_{4,1}$. Considering Table 3.2, there are only two improper point groups with 8 elements that do not contain the inversion. Obviously, of these two, the symmetry group of our molecule is $D_{2d} = \left[\bar{4}2\frac{2}{m}\right]$.

(b) With the multiplication Table B.4 one finds the following class division of the group,

$$D_{2d} = \{E\} \cup \{\delta_2^{\parallel}\} \cup \{\delta_{2,1}^{\perp}, \delta_{2,2}^{\perp}\} \cup \{\rho_1, \rho_2\} \cup \{\sigma_{4,1}, \sigma_{4,2}\}\ .$$

So, it is clear that only E and $\delta_2^{\parallel}$ together can form a normal sub-group H of order 2 (see the criterion at the end of Sect. 2.3.5). The cosets then are

$$\begin{aligned}
L_E &= H \quad (\equiv E \in G/H)\ ,\\
L_{\delta_{2,1}^{\perp}} &= \{L_{\delta_{2,1}^{\perp}}, L_{\delta_{2,2}^{\perp}}\} \quad (\equiv a_1 \in G/H)\ ,\\
L_{\rho_1} &= \{L_{\rho_1}, L_{\rho_2}\} \quad (\equiv a_2 \in G/H)\ ,\\
L_{\sigma_{4,1}} &= \{L_{\sigma_{4,1}}, L_{\sigma_{4,2}}\} \quad (\equiv a_3 \in G/H)\ .
\end{aligned}$$

The elements of the factor group have the algebra

$$a_i^2 = E, a_1 \cdot a_2 = a_3, a_1 \cdot a_3 = a_2, a_2 \cdot a_3 = a_1\ .$$

Hence, the factor group G/H is isomorphic to D_2 (see the multiplication Table 2.3).

Table B.4 Multiplication table for the symmetry group of the molecule in Fig. 3.13

	E	$\delta_2^{\parallel}$	$\delta_{2,1}^{\perp}$	$\delta_{2,2}^{\perp}$	ρ_1	ρ_2	$\sigma_{4,1}$	$\sigma_{4,2}$
E	E	$\delta_2^{\parallel}$	$\delta_{2,1}^{\perp}$	$\delta_{2,2}^{\perp}$	ρ_1	ρ_2	$\sigma_{4,1}$	$\sigma_{4,2}$
$\delta_2^{\parallel}$	$\delta_2^{\parallel}$	E	$\delta_{2,2}^{\perp}$	$\delta_{2,1}^{\perp}$	ρ_2	ρ_1	$\sigma_{4,2}$	$\sigma_{4,1}$
$\delta_{2,1}^{\perp}$	$\delta_{2,1}^{\perp}$	$\delta_{2,2}^{\perp}$	E	$\delta_2^{\parallel}$	$\sigma_{4,2}$	$\sigma_{4,1}$	ρ_2	ρ_1
$\delta_{2,2}^{\perp}$	$\delta_{2,2}^{\perp}$	$\delta_{2,1}^{\perp}$	$\delta_2^{\parallel}$	E	$\sigma_{4,1}$	$\sigma_{4,2}$	ρ_1	ρ_2
ρ_1	ρ_1	ρ_2	$\sigma_{4,1}$	$\sigma_{4,2}$	E	$\delta_2^{\parallel}$	$\delta_{2,1}^{\perp}$	$\delta_{2,2}^{\perp}$
ρ_2	ρ_2	ρ_1	$\sigma_{4,2}$	$\sigma_{4,1}$	$\delta_2^{\parallel}$	E	$\delta_{2,2}^{\perp}$	$\delta_{2,1}^{\perp}$
$\sigma_{4,1}$	$\sigma_{4,1}$	$\sigma_{4,2}$	ρ_1	ρ_2	$\delta_{2,2}^{\perp}$	$\delta_{2,1}^{\perp}$	$\delta_2^{\parallel}$	E
$\sigma_{4,2}$	$\sigma_{4,2}$	$\sigma_{4,1}$	ρ_2	ρ_1	$\delta_{2,1}^{\perp}$	$\delta_{2,2}^{\perp}$	E	$\delta_2^{\parallel}$

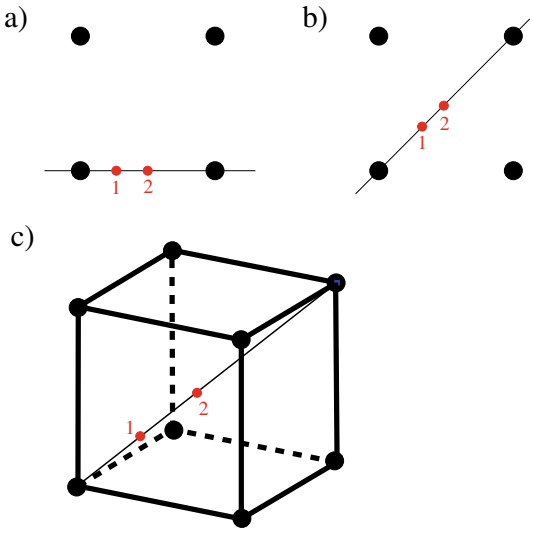

Fig. B.3 The position of an additional atom in a cubic lattice

3. The three cases are shown in Fig. B.3. The respective proper or improper point groups are:

   (a) position 1:
   proper point group: C_4,
   improper point group: C_4+4 mirror planes $= C_{4v}$,
   position 2:
   proper point group D_4,
   improper point group: $D_4 + I = D_{4h}$.

(b) position 1:
proper point group: C_2,
improper point group: C_2+2 mirror planes $= C_{2v}$,
position 2:
proper point group: D_4,
improper point group: $D_4 + I = D_{4h}$.

(c) position 1:
proper point group: C_3,
improper point group: C_3+3 mirror planes $= C_{3v}$,
position 2:
proper point group: O,
improper point group: $O + I = O_h$.

4. (i) D_{4h},
   (ii) D_{2h},
   (iii) D_{3d},
   (iv) C_{2v}.
5. (i) In the case of the group D_2, one possible way is to start from the cuboid with which we illustrated this group in the Chap. 2, and to position an atom on each of the 8 vertices (see Fig. 2.1). There we had ignored consciously the improper symmetries of this body, since its actual point group is D_{2h}. We must now add atoms that preserve the proper symmetry transformations but eliminate the improper ones. Here, it is sufficient to break the inversion symmetry. This succeeds, for example, in the (artificial) molecule in Fig. B.4.
   (ii) The group D_{3h} contains a 6-fold rotation inversion axis, as well as three 2-fold axes of rotation and mirror planes. The inversion is no symmetry operation. This leads to a similar situation as in Fig. B.2, except that the two faces (left and right) must be chosen as regular hexagon (see the six (red) atoms in Fig. B.5).
6. The only symmetry that exists in any 2-dimensional system is the mirror plane. Together with the identity element, this leads to the group C_s.
7. It becomes D_{4h}.

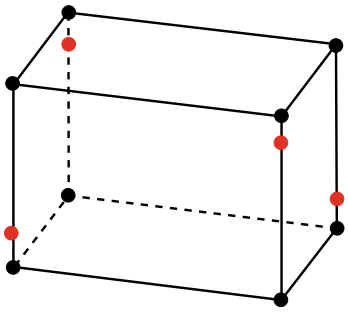

Fig. B.4 An artificial molecule with the symmetry group D_2

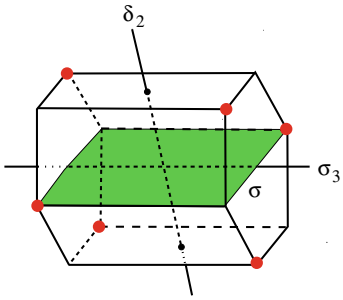

Fig. B.5 An artificial molecule with the symmetry group D_{3h}. Shown are the 6-fold rotation inversion axis (σ_3) and one of the three 2-fold rotation axes (σ_2) and one of the mirror planes σ

8. Given that two point groups are equivalent, there is, then, a matrix $\tilde{S}$ with

$$\tilde{S}^{-1} \cdot \tilde{D}_i \cdot \tilde{S} = \tilde{D}'_i \ ,$$

for all matrices $\tilde{D}_i$, $\tilde{D}'_i$ of the two groups. This equation then obviously also defines the isomorphism $\tilde{D}_i \leftrightarrow \tilde{D}'_i$, because

$$\tilde{D}'_l = \tilde{D}'_i \cdot \tilde{D}'_j = (\tilde{S}^{-1} \cdot \tilde{D}_i \cdot \tilde{S}) \cdot (\tilde{S}^{-1} \cdot \tilde{D}_j \cdot \tilde{S}) = \tilde{S}^{-1} \cdot \tilde{D}_i \cdot \tilde{D}_j \cdot \tilde{S} = \tilde{S}^{-1} \cdot \tilde{D}_l \cdot \tilde{S} \ . \surd$$

9. Suppose that $C_2 \times C_4$ is isomorphic to C_8. Then, there must be a generating element $(a; b) \in C_2 \times C_4$ with $a \in C_2$ and $b \in C_4$ and

$$(a; b)^l = E \ . \tag{B.3}$$

for (and only for) $l = 8$. a and b can be written as $a = a_g^m, b = b_g^n$ with generating elements a_g, b_g and some natural numbers m, n. Then, it follows

$$(a; b)^4 = (a_g^m; b_g^n)^4 = (a_g^{4m}; b_g^{4n}) = (E; E) = E$$

in contradiction to (B.3) , i.e. $C_2 \times C_4$ is not isomorphic to C_8.

Chapter 5

1. (a) If $a_i \sim a'_i$ and $b_j \sim b'_j$ there must be $a \in G_1$ and $b \in G_2$ such that

$$a_i = a^{-1} \cdot a'_i \cdot a \quad \vee \quad b_j = b^{-1} \cdot b'_j \cdot b \quad \Rightarrow \quad (a_i; b_j) = (a; b)^{-1} \cdot (a'_i; b'_j) \cdot (a; b)$$

and therefore $(a_i; b_j) \sim (a'_i; b'_j)$. Since the argument also works in the opposite direction, the assertion holds. Hence, for every pair of classes $\mathcal{C}_k \in G_1$, $\mathcal{C}_l \in G_2$ there exists a class $\mathcal{C}_{[k,l]} \in G_1 \times G_2$ that consists of all pairs (a_i, b_j) with $a_i \in \mathcal{C}_k$, $b_j \in \mathcal{C}_l$. The number of elements in $\mathcal{C}_{[k,l]}$ is $r_{[k,l]} = r_k \cdot r_l$.

(b) The proof of the representation property is straightforward:

$$\begin{aligned}\Gamma^{1\otimes 2}_{(i,j),(k,l)}((a;b)\cdot(a';b')) &= \Gamma^{1\otimes 2}_{(i,j),(k,l)}((a\cdot a';b\cdot b'))\\ &= \Gamma^{1}_{i,k}(a\cdot a')\cdot\Gamma^{2}_{j,l}(b\cdot b')\\ &= \sum_{p,q}\Gamma^{1}_{i,p}(a)\cdot\Gamma^{1}_{p,j}(a')\cdot\Gamma^{2}_{j,q}(b)\cdot\Gamma^{2}_{q,l}(b')\\ &= \sum_{p,q}\Gamma^{1\otimes 2}_{(i,j),(p,q)}((a;b))\cdot\Gamma^{1\otimes 2}_{(p,q),(k,l)}((a';b')).\surd\end{aligned}$$

(c) To show the irreducibility, we use (5.24). We know the number of elements $r_{[i,j]}$ from (a). Then, we need the character (with some elements $a_i \in \mathcal{C}_i, b_j \in \mathcal{C}_j$)

$$\chi_{[i,j]} = \sum_{k,l}\Gamma^{1\otimes 2}_{(k,l),(k,l)}((a_i;b_j)) = \sum_{k,l}\Gamma^{1}_{k,k}(a_i)\cdot\Gamma^{2}_{l,l}(b_j) = \chi^1_i\cdot\chi^2_j\ .$$

Hence, we obtain

$$\sum_{[i,j]} = r_{[i,j]}|\chi_{[i,j]}|^2 = \left(\sum_i r_i|\chi^1_i|\right)\left(\sum_j r_j|\chi^2_j|\right) = g_1\cdot g_2 = g.\surd$$

2. We need the irreducible representations of the two groups D_3 and C_2 given in Tables 4.1 and 6.1. The product matrices then lead to the irreducible representations of D_{3d}, which we give in Table B.5.
3. As always in this context we use (5.23). The characters χ^p_i are given in Table 5.1, those of the three-dimensional orthogonal matrices can be calculated with (3.5). For the group D_2 one finds

$$\chi(E) = 3,\ \chi(\delta_{2,i}) = -1\ .$$

Thus, it is

$$\begin{aligned}n_A &= \frac{1}{4}(1\cdot 1\cdot 3 + 1\cdot 1\cdot(-1) + 1\cdot 1\cdot(-1) + 1\cdot 1\cdot(-1))\ ,\\ &= \frac{1}{4}(3-1-1-1) = 0\ ,\\ n_{B_1} &= \frac{1}{4}(3+1+1-1) = 1 = n_{B_2} = n_{B_3}\ ,\end{aligned}$$

and

$$\Gamma = \Gamma^{B_1}\oplus\Gamma^{B_2}\oplus\Gamma^{B_3}\ .$$

Table B.5 Irreducible representations of the group D_{3d}. The matrices $\tilde{D}_i$ are defined in (2.16)

	E	δ_3	δ_3^2	δ_{21}	δ_{22}	δ_{23}	I	$(I\delta_3)$	$(I\delta_3^2)$	$(I\delta_{21})$	$I\delta_{22})$	$I\delta_{23})$
$\Gamma^{A\otimes A}$	1	1	1	1	1	1	1	1	1	1	1	1
$\Gamma^{A\otimes B}$	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1
$\Gamma^{A\otimes E}$	$\tilde{D}_1$	$\tilde{D}_2$	$\tilde{D}_3$	$\tilde{D}_4$	$\tilde{D}_5$	$\tilde{D}_6$	$\tilde{D}_1$	$\tilde{D}_2$	$\tilde{D}_3$	$\tilde{D}_4$	$\tilde{D}_5$	$\tilde{D}_6$
$\Gamma^{B\otimes A}$	1	1	1	-1	-1	-1	1	1	1	-1	-1	-1
$\Gamma^{B\otimes B}$	-1	-1	-1	1	1	1	-1	-1	-1	1	1	1
$\Gamma^{B\otimes E}$	$\tilde{D}_1$	$\tilde{D}_2$	$\tilde{D}_3$	$\tilde{D}_4$	$\tilde{D}_5$	$\tilde{D}_6$	$-\tilde{D}_1$	$-\tilde{D}_2$	$-\tilde{D}_3$	$-\tilde{D}_4$	$-\tilde{D}_5$	$-\tilde{D}_6$

For the group D_3 the relevant characters are

$$\chi(E) = 3, \chi(\delta_3) = \chi(\delta_3^2) = 0, \chi(\delta_{2,i}) = -1 \ .$$

Hence,

$$\begin{aligned} n_{A_1} &= \frac{1}{6}(1 \cdot 1 \cdot 3 + 2 \cdot 0 \cdot (-1) + 3 \cdot 1 \cdot (-1)) = 0 \ , \\ n_{A_2} &= \frac{1}{6}(3 + 0 + 3) = 1 \ , \\ n_E &= \frac{1}{6}(6 + 0 + 0) = 1 \ , \end{aligned}$$

i.e.

$$\Gamma = \Gamma^{A_2} \oplus \Gamma^E \ .$$

4. We use (5.23). In this case, all characters (χ_i^p and χ) are given in Tables 5.1 and 6.1.

   (a) $G' = \{E, \delta_3, \delta_3^2\} \widehat{=} C_3$

   (i) $\bar{\Gamma}^{(s)} = A_1$:

$$\begin{aligned} n_A &= \frac{1}{3}(1 + 1 + 1) = 1 \ , \\ n_{E_1} &= \frac{1}{3}(1 + \underbrace{\omega + \omega^2}_{-1}) = 0 = n_{E_2} \ . \end{aligned}$$

   Hence

$$A_1 \to A \ .$$

   (ii) $\bar{\Gamma}^{(s)} = A_2$: same result as in (i),

$$A_2 \to A \ .$$

(iii) $\bar{\Gamma}^{(s)} = E$:

$$n_A = \frac{1}{3}(2-2) = 0 \,,$$
$$n_{E_1} = \frac{1}{3}(2-\omega-\omega^2) = 1 = n_{E_2} \,.$$

Hence

$$E \to E_1 \oplus E_2 \,.$$

(b) $G' = \{E, \delta_{2,x}\} \mathrel{\widehat{=}} C_2$
(i) $\bar{\Gamma}^{(s)} = A_1$:

$$n_A = \frac{1}{2}(1+1) = 1 \,,$$
$$n_B = \frac{1}{2}(1-1) = 0 \,.$$

Hence,

$$A_2 \to A \,.$$

(ii) $\bar{\Gamma}^{(s)} = A_2$:

$$n_A = \frac{1}{2}(1-1) = 0 \,,$$
$$n_B = \frac{1}{2}(1+1) = 1 \,.$$

Hence,

$$A_2 \to B \,.$$

(iii) $\bar{\Gamma}^{(s)} = E$:

$$n_A = \frac{1}{2}(1+1) = 1 \,,$$
$$n_B = \frac{1}{2}(1+1) = 1 \,.$$

Hence,

$$E \to A \oplus B \,.$$

5. We take the sum over $i = j$ and $l = k$ in (5.2),

$$\sum_{a\in G}\chi(a)\cdot\chi(a)^* = \sum_{a\in G}|\chi(a)|^2 = \frac{g}{d}\sum_{i,l}\delta_{i,j}\delta_{l,k}\delta_{i,l}\delta_{j,k} = \frac{g}{d}\underbrace{\sum_{i}1}_{=d} = g\ .$$

Since the characters $\chi(a)$ are identical in a class, we obtain (5.24) and thus $\bar{\Gamma}$ is irreducible.

6. In order to evaluate (5.24), we need the characters of the 6 matrices,

$$\chi(E) = 3\ ,\ \chi(\delta_3) = \chi(\delta_2^3) = 0\ ,\ \chi(\delta_{21}) = \chi(\delta_{22}) = \chi(\delta_{23}) = 1\ .$$

Then, the left side of (5.24) becomes

$$1\cdot 3^2 + 2\cdot 0^2 + 3\cdot 1^2 = 12\ (\neq g = 6)\ .$$

Hence, this representation is reducible. With (5.23) and Table 4.1 we obtain the numbers

$$\begin{aligned} n_{A_1} &= \frac{1}{6}(1\cdot 3\cdot 1 + 2\cdot 0\cdot 1 + 3\cdot 1\cdot 1) = 1\ , \\ n_{A_2} &= \frac{1}{6}(1\cdot 3\cdot 1 + 2\cdot 0\cdot 1 + 3\cdot 1\cdot (-1)) = 0\ , \\ n_{E} &= \frac{1}{6}(1\cdot 3\cdot 2 + 2\cdot 0\cdot (-1) + 3\cdot 1\cdot 0) = 1\ . \end{aligned}$$

Hence, $\bar{\Gamma} = \bar{\Gamma}^A \otimes \bar{\Gamma}^E$.

7. As we have shown in Sect. 4.1.1, every representation is equivalent to a unitary one. Since the characters of two equivalent representations are identical, we can consider a unitary representation ($\tilde{\Gamma}^{-1}(a) = \tilde{\Gamma}^{\dagger}(a)$). Then, the statement follows immediately:

$$\chi(a^{-1}) = \sum_i [\tilde{\Gamma}(a^{-1})]_{i,i} = \sum_i [\tilde{\Gamma}(a)^{-1}]_{i,i} = \sum_i [\tilde{\Gamma}(a)^{\dagger}]_{i,i} = \sum_i [\tilde{\Gamma}(a)]^*_{i,i} = \chi(a)^*.\surd$$

8. If we choose the representations $p' = 1$ ($\Gamma^{p'}(a) = 1\ \forall\ a$) and $p \neq 1$ in the orthogonality theorem (5.1) or (5.2), it then follows immediately

$$\sum_{a\in G}\Gamma^p_{i,j}(a)\Gamma^{p'}_{k,l}(a^{-1}) = \sum_{a\in G}\Gamma^p_{i,j}(a) = 0.\surd$$

9. Because of (4.20), the irreducible representations must be one-dimensional. Furthermore, according to Theorem 1, each element is its own class. Now, let G be non-Abelian. Then, there are at least two elements a, b with

$$a\cdot b = c \neq d = b\cdot a\ .$$

However, for some one-dimensional representation $\bar{\Gamma}^p$ it applies

$$\Gamma^p(c) = \Gamma^p(a) \cdot \Gamma^p(b) = \Gamma^p(b) \cdot \Gamma^p(a) = \Gamma^p(d)$$

i.e. the two different group elements c and d have the same character in each representation. This contradicts the orthogonality theorem (5.9) and therefore G must be Abelian. $\surd$

10. For both elements $a = I$ or $a = \sigma$ it applies $a^2 = E$, hence

$$\Gamma(a^2) = \Gamma(a)^2 = \Gamma(E) = 1 \ .$$

Thus it is $\Gamma(a) = \pm\tilde{1}$. $\surd$

11. In a non-Abelian group there are at least two group elements a, b for which

$$a \cdot b \neq b \cdot a$$

applies. This means that

$$a \cdot b \cdot a^{-1} \neq b$$

and there must therefore be an element

$$c \equiv a \cdot b \cdot a^{-1} \neq b$$

that is in the same class as b. Hence, there would be at least one class with more than one element. If there were only one-dimensional representations, however, all classes would have to consist of only one element according to (5.24) and Theorem 1 in Sect. 4.2. This contradicts our above finding and therefore there cannot be only one-dimensional representations. $\surd$

Chapter 6

1. To use (6.14), we need the effect of the rotations in C_3 on a vector $\vec{r}$. With (3.3) we find for δ_3 ($\varphi = \frac{2\pi}{3}$)

$$\begin{aligned} x &\to -\frac{x}{2} - \frac{\sqrt{3}}{2} y \ , \\ y &\to \frac{\sqrt{3}}{2} x - \frac{y}{2} \ , \\ z &\to z \ , \end{aligned}$$

and for δ_3^2 ($\varphi = \frac{4\pi}{3}$)

$$x \to -\frac{x}{2} + \frac{\sqrt{3}}{2}y \,,$$
$$y \to -\frac{\sqrt{3}}{2}x - \frac{y}{2} \,,$$
$$z \to z \,.$$

Hence, we obtain (see (6.2)),

$$\hat{T}_{\delta_3}(x \cdot y) = \left(-\frac{x}{2} - \frac{\sqrt{3}}{2}y\right)\left(\frac{\sqrt{3}}{2}x - \frac{y}{2}\right) = -\frac{\sqrt{3}}{4}x^2 - \frac{x \cdot y}{2} + \frac{\sqrt{3}}{4}y^2 \,,$$
$$\hat{T}_{\delta_3^2}(x \cdot y) = \frac{\sqrt{3}}{4}x^2 - \frac{x \cdot y}{2} - \frac{\sqrt{3}}{4}y^2 \,.$$

With this result, we can now apply the projection operators (6.14) to the state $\Psi(\vec{r})$:

$$\begin{aligned}
\hat{P}^A\Psi(\vec{r}) &= \frac{f(\vec{r})}{3}(\hat{T}_E \cdot x \cdot y + \hat{T}_{\delta_3} \cdot x \cdot y + \hat{T}_{\delta_3^2} \cdot x \cdot y) \\
&= \frac{f(\vec{r})}{3}\left(x \cdot y - \frac{x \cdot y}{2} - \frac{x \cdot y}{2}\right) = 0 \,, \\
\hat{P}^{E_1}\Psi(\vec{r}) &= \frac{f(\vec{r})}{3}(\hat{T}_E \cdot (x \cdot y) + \omega\hat{T}_{\delta_3} \cdot (x \cdot y) + \omega^2\hat{T}_{\delta_3^2} \cdot (x \cdot y)) \\
&= \frac{f(\vec{r})}{3}\left(x \cdot y + \frac{\sqrt{3}}{4}\underbrace{(\omega^2 - \omega)}_{-\sqrt{3}\mathrm{i}}x^2 - \frac{x \cdot y}{2}\underbrace{(\omega + \omega^2)}_{=-1} + \frac{\sqrt{3}}{4}(\omega^2 - \omega)y^2\right) \\
&= f(\vec{r})\frac{\mathrm{i}}{4}(x + \mathrm{i}y)^2 \equiv \Psi_{E_1}(\vec{r}) \,, \\
\hat{P}^{E_2}\Psi(\vec{r}) &= f(\vec{r})\frac{\mathrm{i}}{4}(x - \mathrm{i}y)^2 \equiv \Psi_{E_2}(\vec{r}) \,.
\end{aligned}$$

Hence, we find

$$\Psi(\vec{r}) = \Psi_{E_1}(\vec{r}) + \Psi_{E_2}(\vec{r}) \,.$$

2. (a) The group C_{3v} has the 6 elements $\{E, \delta_3, \delta_3^2, \sigma_1, \sigma_2, \sigma_3\}$ where the three mirror planes are displayed in Fig. B.6. Like in Sect. 6.3.5, we can start again from the state $|1\rangle$ and construct a basis of the representation spaces

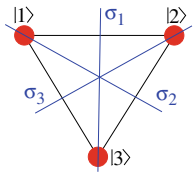

Fig. B.6 A molecule with a triangular shape

of C_{3v} using the operators $\hat{P}^{p}_{\lambda,\lambda}$,

$$\begin{aligned}\hat{P}^{A_1}_{1,1}|1\rangle &= \frac{1}{6}\left(\hat{T}_E|1\rangle + \hat{T}_{\delta_3}|1\rangle + \hat{T}_{\delta_3^2}|1\rangle + \hat{T}_{\sigma_1}|1\rangle + \hat{T}_{\sigma_2}|1\rangle + \hat{T}_{\sigma_3}|1\rangle\right)\\ &= \frac{1}{6}\left(|1\rangle + |2\rangle + |3\rangle + |2\rangle + |1\rangle + |3\rangle\right)\\ &= \frac{1}{3}\left(|1\rangle + |2\rangle + |3\rangle\right) \equiv \sqrt{3}|\Psi^{A_1}\rangle\end{aligned}$$

where the state $|\Psi^{A_1}\rangle$ is normalized. For the 3 other operators we find

$$\begin{aligned}\hat{P}^{A_2}_{1,1}|1\rangle &= \frac{1}{6}\left(\hat{T}_E|1\rangle + \hat{T}_{\delta_3}|1\rangle + \hat{T}_{\delta_3^2}|1\rangle - \hat{T}_{\sigma_1}|1\rangle - \hat{T}_{\sigma_2}|1\rangle - \hat{T}_{\sigma_3}|1\rangle\right) = 0\ ,\\ \hat{P}^{E}_{1,1}|1\rangle &= \frac{2}{6}\left(\hat{T}_E|1\rangle + \omega\hat{T}_{\delta_3}|1\rangle + \omega^2\hat{T}_{\delta_3^2}|1\rangle\right)\\ &= \frac{2}{6}\left(|1\rangle + \omega|2\rangle + \omega^2|3\rangle\right) \equiv \sqrt{3}|\Psi^{E}_1\rangle\ ,\\ \hat{P}^{E}_{2,2}|1\rangle &= \frac{2}{6}\left(|1\rangle + \omega^2|2\rangle + \omega|3\rangle\right) \equiv \sqrt{3}|\Psi^{E}_2\rangle\ .\end{aligned}$$

Because of our findings in Sect. 6.3.5, the Hamiltonian must be diagonal with respect to the three basis states $|\Psi^{A_1}\rangle$, $|\Psi^{E}_{1,1}\rangle$, $|\Psi^{E}_{2,2}\rangle$ with diagonal elements

$$\begin{aligned}\langle\Psi^{A_1}|\hat{H}|\Psi^{A_1}\rangle &= 2t\ ,\\ \langle\Psi^{E}_1|\hat{H}|\Psi^{E}_1\rangle &= \langle\Psi^{E}_2|\hat{H}|\Psi^{E}_2\rangle = -t\ .\end{aligned} \tag{B.4}$$

Note that (B.4) confirms our general finding (6.23).

(b) With the 3 states $|4\rangle$, $|5\rangle$, $|6\rangle$ we can define analogously

$$\begin{aligned}|\tilde{\Psi}^{A_1}\rangle &= \frac{1}{\sqrt{3}}(|4\rangle + |5\rangle + |6\rangle)\ ,\\ |\tilde{\Psi}^{E}_1\rangle &= \frac{1}{\sqrt{3}}(|4\rangle + \omega|5\rangle + \omega^2|6\rangle)\ ,\\ |\tilde{\Psi}^{E}_2\rangle &= \frac{1}{\sqrt{3}}(|4\rangle + \omega^2|5\rangle + \omega|6\rangle)\ .\end{aligned}$$

In the basis of the 6 states $|\Psi^{A_1}\rangle, \ldots, |\tilde{\Psi}^{E}_2\rangle$ the Hamiltonian is block-diagonal with 2×2 blocks of states $\{|\Psi^{A_1}\rangle, |\tilde{\Psi}^{A_1}\rangle\}$, $\{|\Psi^{E}_i\rangle, |\tilde{\Psi}^{E}_i\rangle\}$. The off-diagonal elements are

$$\langle\Psi^{A_1}|\hat{H}|\tilde{\Psi}^{A_1}\rangle = \langle\tilde{\Psi}^{E}_i|\hat{H}|\Psi^{E}_i\rangle = t'\ .$$

Thus, the Hamiltonian matrix has the form

$$\tilde{H} = \begin{pmatrix} 2t & t' & 0 & 0 & 0 & 0 \\ t' & 2t & 0 & 0 & 0 & 0 \\ 0 & 0 & -t & t' & 0 & 0 \\ 0 & 0 & t' & -t & 0 & 0 \\ 0 & 0 & 0 & 0 & -t & t' \\ 0 & 0 & 0 & 0 & t' & -t \end{pmatrix}$$

with eigenstates

$$|\Psi_{\pm}^{A_1}\rangle = |\Psi^{A_1}\rangle \pm |\tilde{\Psi}^{A_1}\rangle \ ,$$
$$|\Psi_{i,\pm}^{E}\rangle = |\Psi_i^{E}\rangle \pm |\tilde{\Psi}_i^{E}\rangle \ .$$

(c) For l triangles, the Hamiltonian matrix is obviously block diagonal with l-dimensional sub-matrices. This corresponds to the problem of three decoupled one-dimensional chains with the Hamiltonians

$$\hat{H}^{\text{chains}} = \epsilon \sum_i |i\rangle\langle i| - t' \sum_{\langle i,j\rangle} |i\rangle\langle j| \ ,$$

where $\epsilon = 2t$ or $\epsilon = -t$ and $\langle i, j\rangle$ is a sum over nearest neighbors.

3. With the definition (6.14) (with $\lambda = \lambda'$) of the projection operators we find

$$\begin{aligned} \hat{P}_{\lambda,\lambda}^{p} \cdot \hat{P}_{\lambda',\lambda'}^{p'} &= \frac{d_p \cdot d_{p'}}{g^2} \sum_{a,a'} \left(\Gamma_{\lambda,\lambda}^{p}(a)\right)^* \left(\Gamma_{\lambda',\lambda'}^{p'}(a')\right)^* \hat{U}_{a\cdot a'} \\ &\overset{(b\equiv a\cdot a')}{=} \frac{d_p \cdot d_{p'}}{g^2} \sum_{a,b} \left(\Gamma_{\lambda,\lambda}^{p}(a)\right)^* \left(\Gamma_{\lambda',\lambda'}^{p'}(a^{-1}\cdot b)\right)^* \hat{U}_b \\ &= \frac{d_p \cdot d_{p'}}{g^2} \sum_{a,b} \sum_{\lambda''} \left(\Gamma_{\lambda,\lambda}^{p}(a)\right)^* \left(\Gamma_{\lambda',\lambda''}^{p'}(a^{-1})\right)^* \left(\Gamma_{\lambda'',\lambda'}^{p'}(b)\right)^* \hat{U}_b \\ &\overset{(5.1)}{=} \delta_{p,p'}\delta_{\lambda\lambda'} \frac{d_p}{g} \sum_{b} \left(\Gamma_{\lambda,\lambda}^{p'}(b)\right)^* \hat{U}_b \\ &= \delta_{p,p'}\delta_{\lambda\lambda'} \hat{P}_{\lambda,\lambda}^{p} \quad \cdot \surd \end{aligned}$$

4. We can express the operator $\hat{P}^p$ by the operators $\hat{P}_{\lambda,\lambda}^{p}$, because

$$\hat{P}^p = \frac{d_p}{g} \sum_a \left(\chi^p(a)\right)^* \hat{U}_a = \frac{d_p}{g} \sum_a \sum_\lambda \left(\Gamma_{\lambda,\lambda}^{p}\right)^* \hat{U}_a = \sum_\lambda \hat{P}_{\lambda,\lambda}^{p} \ . \tag{B.5}$$

(a) We have to show that (i) $\left(\hat{P}^p\right)^\dagger = \hat{P}^p$ and (ii) $\left(\hat{P}^p\right)^2 = \hat{P}^p$. The first defining property is then obviously fulfilled because of (B.5) and the fact that the operator $\hat{P}_{\lambda,\lambda}^{p}$ is Hermitian. The second one follows from

$$\left(\hat{P}^p\right)^2 = \sum_{\lambda,\lambda'} \hat{P}^p_{\lambda,\lambda} \hat{P}^p_{\lambda',\lambda'} = \sum_{\lambda} \hat{P}^p_{\lambda,\lambda} = \hat{P}^p$$

where the second equation follows from Exercise 3 and $(\hat{P}^p_{\lambda,\lambda})^2 = \hat{P}^p_{\lambda,\lambda}$.

(b) The statement follows directly from (B.5) and the properties of the operators $\hat{P}^p_{\lambda,\lambda}$, which we have discussed in Sect. 6.2.

Chapter 7

1. As an example, we consider the rotation by an angle $\pi/2$. These have the following effect on the two basis states

$$\hat{U}_{\pi/2}|p_x\rangle = |p_y\rangle \quad , \quad \hat{U}_{\pi/2}|p_y\rangle = -|p_x\rangle \; .$$

Then we find

$$\begin{aligned}\hat{U}_{\pi/2} \cdot \hat{H} \cdot \hat{U}^\dagger_{\pi/2} &= \varepsilon \left(\hat{U}_{\pi/2}|p_x\rangle\langle p_x|\hat{U}^\dagger_{\pi/2} + \hat{U}_{\pi/2}|p_y\rangle\langle p_y|\hat{U}^\dagger_{\pi/2}\right) \\ &\quad + \mathrm{i}\Omega \left(\hat{\mathrm{U}}_{\pi/2}|\mathrm{p_x}\rangle\langle \mathrm{p_y}|\hat{\mathrm{U}}^\dagger_{\pi/2} - \hat{\mathrm{U}}_{\pi/2}|\mathrm{p_y}\rangle\langle \mathrm{p_x}|\hat{\mathrm{U}}^\dagger_{\pi/2}\right) \\ &= \varepsilon \left(|p_y\rangle\langle p_y| + |p_x\rangle\langle p_x|\right) + \mathrm{i}\Omega \left(-|p_y\rangle\langle p_x| + |p_x\rangle\langle p_y|\right) = \hat{H} \quad .\surd\end{aligned}$$

The same holds for the two other rotations $\hat{U}_\pi$ and $\hat{U}_{3\pi/2}$.

2. We go through all classes of O_h, see Table 7.1, and determine for each element $\hat{U}_a$ of the class

$$\chi(a) = \langle \Psi^{[1,1,3]}_2 | \hat{U}_a | \Psi^{[1,1,3]}_2 \rangle + \langle \Psi^{[1,1,3]}_3 | \hat{U}_a | \Psi^{[1,1,3]}_3 \rangle \; .$$

(i) $a = E$: Here it is obviously $\chi(a) = 2$.

(ii) $a \in 6C_4$, e.g. $a = \delta_{4,z}$, i.e.

$$x_1 \to x_2, \; x_2 \to -x_1, \; x_3 \to x_3$$

$\Rightarrow$

$$\begin{aligned}\hat{U}_a|\Psi^{[1,1,3]}_2\rangle &= -|\Psi^{[1,1,3]}_2\rangle \; , \\ \hat{U}_a|\Psi^{[1,1,3]}_3\rangle &= |\Psi^{[1,1,3]}_3\rangle \; , \\ &\to \chi(a) = 0 \; .\end{aligned}$$

(iii) $a \in 3C_4^2$, e.g. $a = \delta_{2,z}$, i.e.

$$x_1 \to -x_1, \; x_2 \to -x_2, \; x_3 \to x_3$$

$\Rightarrow$

$$\begin{aligned}\hat{U}_a|\Psi_2^{[1,1,3]}\rangle &= |\Psi_2^{[1,1,3]}\rangle \ , \\ \hat{U}_a|\Psi_3^{[1,1,3]}\rangle &= |\Psi_3^{[1,1,3]}\rangle \ , \\ &\rightarrow \chi(a) = 2 \ .\end{aligned}$$

(iv) $a \in 8C_3$, e.g. a rotation axis $a = (1, 1, 1)^T$, i.e.

$$x_3 \rightarrow x_1, \ x_1 \rightarrow x_2, \ x_2 \rightarrow x_3$$

$\Rightarrow$

$$\begin{aligned}\hat{U}_a|\Psi_2^{[1,1,3]}\rangle &= \frac{1}{\sqrt{2}}(\Psi_{1,3,1} - \Psi_{1,1,3}), \\ \hat{U}_a|\Psi_3^{[1,1,3]}\rangle &= \frac{1}{\sqrt{6}}(2\Psi_{3,1,1} - \Psi_{1,1,3} - \Psi_{1,3,1}) \ , \\ &\rightarrow \chi(a) = -1 \ .\end{aligned}$$

(v) $a \in 6C_2'$, e.g. a rotation axis $a = (1, 0, 1)^T$, i.e.

$$x_3 \rightarrow x_1, \ x_2 \rightarrow -x_2, \ x_1 \rightarrow x_3$$

$\Rightarrow$

$$\begin{aligned}\hat{U}_a|\Psi_2^{[1,1,3]}\rangle &= \frac{1}{\sqrt{2}}(\Psi_{1,1,3} - \Psi_{1,3,1}), \\ \hat{U}_a|\Psi_3^{[1,1,3]}\rangle &= \frac{1}{\sqrt{6}}(2\Psi_{3,1,1} - \Psi_{1,3,1} - \Psi_{1,1,3}) \ , \\ &\rightarrow \chi(a) = 0 \ .\end{aligned}$$

All other classes in Table 7.1 result from the discussed ones by multiplication with the inversion. Since

$$\hat{I}|\Psi_2^{[1,1,3]}\rangle = |\Psi_2^{[1,1,3]}\rangle \ , \quad \hat{I}|\Psi_3^{[1,1,3]}\rangle = |\Psi_3^{[1,1,3]}\rangle$$

the same characters result. Thus, we have shown that the states $|\Psi_2^{[1,1,3]}\rangle$, $|\Psi_3^{[1,1,3]}\rangle$ have exactly the characters of the irreducible representation E_g in the Table 7.1.

3. We consider the first 5 eigenspaces

   (i) Energy $E = \alpha(2 + \pi)$,

   $$\Psi_{111}(\vec{r}) \sim \cos(x)\cos(y)\cos(z) \ ,$$

   transforms like the representation A_{1g}.

   (ii) Energy $E = \alpha(5 + \pi)$,

   $$\Psi_{2,1,1}(\vec{r}) \sim \sin(x)\cos(y)\cos(z) \ ,$$
   $$\Psi_{1,2,1}(\vec{r}) \sim \cos(x)\sin(y)\cos(z) \ ,$$

   transforms like the representation E_u.

   (iii) Energy $E = \alpha(8 + \pi)$,

   $$\Psi_{221}(\vec{r}) \sim \sin(x)\sin(y)\cos(z),$$

   transforms like the representation B_{2g}.

   (iv) Energy $E = \alpha(10 + \pi)$,

   $$\Psi_{3,1,1}(\vec{r}) \sim \cos(3x)\cos(y)\cos(z) \ ,$$
   $$\Psi_{1,3,1}(\vec{r}) \sim \cos(x)\cos(3y)\cos(z) \ .$$

   These two states do not transform like any two-dimensional representation of D_{4h}. Obviously, however, the linear combination

   $$\Psi_1^{[1,3,1]} \equiv \Psi_{3,1,1} + \Psi_{1,3,1}$$

   transforms like A_{1g}. Therefore, the state

   $$\Psi_2^{[1,3,1]} \equiv \Psi_{3,1,1} - \Psi_{1,3,1} \sim (\cos(3x)\cos(y) - \cos(x)\cos(3y))\cos(z) \ ,$$

   which is orthogonal to $\Psi_1^{[1,3,1]}$, must belong to another one-dimensional eigenspace. It turns out that it transforms like the representation B_{1g}.

   (v) Energy $E = \alpha(2 + 4\pi)$,

   $$\Psi_{112}(\vec{r}) \sim \cos(x)\cos(y)\sin(z) \ ,$$

   transforms like A_{2u}.

4. The new operator has the same symmetry group O_h as that of the unperturbed Hamiltonian operator. Since the first 3 eigenspaces belong to different representations, the Hamiltonian matrix is diagonal and the diagonal elements of the same representations are identical, as shown in Sect. 6.3.5.

5. We only have to show that the traces of the rotation matrices in each class are identical to the one given in Table 7.1 for the representation T_{1u}. For the proper rotations, the trace results from (3.5).

   (i) $a = E$: $\chi(a) = 3$.
   (ii) $a \in 6C_4$: $\chi(a) = 2\cos(\pi/2) + 1 = 1$.
   (iii) $a \in 3C_4^2$: $\chi(a) = 2\cos(\pi) + 1 = -1$.
   (iv) $a \in 8C_3$: $\chi(a) = 2\cos(2\pi/3) + 1 = 0$.
   (v) $a \in 6C_2'$: $\chi(a) = 2\cos(\pi) + 1 = -1$.

   All other classes result from the discussed ones by multiplication with the inversion, which simply leads to a minus sign. $\surd$

Chapter 8

1. The characteristic polynomial is

$$\begin{vmatrix} -\lambda & t & t & t \\ t & -\lambda & t & t \\ t & t & -\lambda & t \\ t & t & t & -\lambda \end{vmatrix} = (\lambda - 3t)(\lambda + 1)^3 \ .$$

   The eigenvector to the eigenvalue $\lambda = 3t$ is

$$|\Psi_1\rangle = \frac{1}{\sqrt{4}}(|1\rangle + |2\rangle + |3\rangle + |4\rangle) \ .$$

   The three degenerate eigenstates to the eigenvalue $\lambda = -t$ are, e.g.

$$\begin{aligned} |\Psi_2\rangle &= \frac{1}{\sqrt{4}}(|1\rangle + |2\rangle - |3\rangle - |4\rangle) \ , \\ |\Psi_3\rangle &= \frac{1}{\sqrt{4}}(|1\rangle - |2\rangle - |3\rangle + |4\rangle) \ , \\ |\Psi_3\rangle &= \frac{1}{\sqrt{4}}(|1\rangle - |2\rangle + |3\rangle - |4\rangle) \ . \end{aligned} \tag{B.6}$$

   The state $|\Psi_1\rangle$ obviously belongs to the representation A_1. The symmetry group T_d of the system has the two three-dimensional representations T_1 and T_2. To find out to which of the two the three states (B.6) belong, we can consider how they behave with respect to mirror plane transformations. For example, the mirror plane in Fig. B.7 leads to

$$\begin{matrix} |1\rangle \\ |2\rangle \\ |3\rangle \\ |4\rangle \end{matrix} \quad \xrightarrow{\hat{T}_\rho} \quad \begin{matrix} |1\rangle \\ |3\rangle \\ |2\rangle \\ |4\rangle \end{matrix} \ .$$

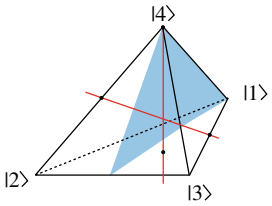

Fig. B.7 Symmetries of a molecular sphere with tetrahedron shape

Hence

$$\langle\Psi_2|\hat{T}_\rho|\Psi_2\rangle = \langle\Psi_4|\hat{T}_\rho|\Psi_4\rangle = 0\ ,$$
$$\langle\Psi_3|\hat{T}_\rho|\Psi_3\rangle = 1\ ,$$

and we find

$$\chi(\hat{T}_\rho) = \sum_i \langle\Psi_i|\hat{T}_\rho|\Psi_i\rangle = 1\ ,$$

which shows that the three states transform like the representation T_2.
If one of the hopping parameters is different, the Hamiltonian matrix is given as

$$\begin{pmatrix} 0 & t & t & t' \\ t & 0 & t & t \\ t & t & 0 & t \\ t' & t & t & 0 \end{pmatrix}\ .$$

Its eigenvalues are

$$-t, -t', t + t' \pm \sqrt{17t^2 - 2tt' + (t')^2}$$

i.e. there is no degeneracy anymore. This is compatible with the fact that the symmetry group of the modified molecule is C_{2v} which only has one-dimensional representations. A look into the correlation tables reveals the splitting

$$T_2 \overset{T_d \to C_{2v}}{\longrightarrow} A_1 \oplus B_1 \oplus B_2\ .$$

2. (a) With an appropriate choice of the function f, lines as in Fig. B.8 could result on which the potential has a constant absolute value. With this figure, one may recognize that the proper point group here is D_2. In addition, there is the inversion and there are three mirror planes, two depicted in green (and dashed), and z=0. This means that the point group is D_{2h}.

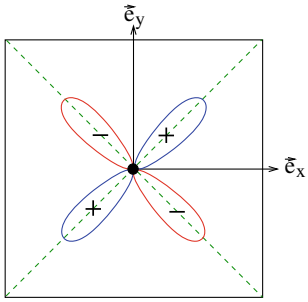

Fig. B.8 Illustration of the symmetry generated by the potential in Exercise 2

(b) According to the correlation tables, the splittings are

$$\underline{V}^{(2)} : T_{2u} \longrightarrow B_{1u} \oplus B_{2u} \oplus B_{3u} \ ,$$
$$\underline{V}^{(3)} : T_{2g} \longrightarrow B_{1g} \oplus B_{2g} \oplus B_{3g} \ .$$

(c) Since all eigenstates in $\underline{V}^{(2)}$ and $\underline{V}^{(3)}$ belong to different representations of D_{2h}, all matrix elements must be zero.

3. (a) In Sect. 7.2 we explained why the system without the delta potential has a higher symmetry than O_h because the Hamiltonian (7.4) is a sum of operators which belong to the three spatial directions. With the addition of the delta potential, this is no longer the case and the maximum symmetry group of the system is therefore O_h.

(b) For the degenerate perturbation theory we need the nine matrix elements built with the states (7.8)–(7.10). Since all three functions have the same value at the origin, all matrix elements are the same. Hence, we have to diagonalize the matrix

$$\tilde{V} = V_0/N \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \ ,$$

where $1/\sqrt{N}$ normalizes the states (7.8)–(7.10). As one can easily show, the eigenvalues of this matrix are $V_1 = 3V_0/N$, $V_2 = 0$, $V_3 = 0$ with eigenstates given in (7.11)–(7.13).

4. The point groups are (a) D_{3d} and (b) D_{6h}.
The reduction of $\Gamma^{(s)}_{l=2}$ is done as always with (5.23). For this, we only need to determine the characters χ_i with (8.4) and (8.5), while χ^p_i and r_i can be found in the character tables of the groups D_{3h} and D_{6h}.

(a) We discuss this case in more detail. The required characters are

$$\begin{aligned}\chi(E) &= (2l+1) = 5\ ,\\ \chi(C_3) &= \frac{\sin\left(\frac{1}{2}\cdot\frac{2\pi}{3}\right)}{\sin\left(\frac{2\pi}{6}\right)} = -1\ ,\\ \chi(C_2) &= 1\ ,\\ \chi(\sigma_{v,h}) &= 1\ ,\\ \chi(S_3) &= 1\ .\end{aligned}$$

Then, (5.23) yields

$$\begin{aligned}n_{A_1'} &= \frac{1}{12}(1\cdot 5\cdot 1+2\cdot(-1)\cdot 1+3\cdot 1\cdot 1+1\cdot 1\cdot 1+2\cdot 1\cdot 1+3\cdot 1\cdot 1) = 1\ ,\\ n_{A_1''} &= \frac{1}{12}(1\cdot 5\cdot 1+2\cdot(-1)\cdot 1+3\cdot 1\cdot 1+1\cdot 1\cdot(-1)+2\cdot 1\cdot(-1)+3\cdot 1\cdot(-1)) = 0\ ,\\ n_{A_2'} &= \frac{1}{12}(1\cdot 5\cdot 1+2\cdot(-1)\cdot 1+3\cdot 1\cdot(-1)+1\cdot 1\cdot 1+2\cdot 1\cdot 1+3\cdot 1\cdot(-1)) = 0\ ,\\ n_{A_2''} &= \frac{1}{12}(1\cdot 5\cdot 1+2\cdot(-1)\cdot 1+3\cdot 1\cdot(-1)+1\cdot 1\cdot(-1)+2\cdot 1\cdot(-1)+3\cdot 1\cdot 1) = 0\ ,\\ n_{E'} &= \frac{1}{12}(1\cdot 5\cdot 2+2\cdot(-1)\cdot(-1)+3\cdot 1\cdot 0+1\cdot 1\cdot 2+2\cdot 1\cdot(-1)+3\cdot 1\cdot 0) = 1\ ,\\ n_{E''} &= \frac{1}{12}(1\cdot 5\cdot 2+2\cdot(-1)\cdot(-1)+3\cdot 1\cdot 0+1\cdot 1\cdot(-2)+2\cdot 1\cdot 1+3\cdot 1\cdot 0) = 1\ .\end{aligned}$$

Hence,

$$\Gamma^{(s)}_{l=2} = A_1' \oplus E' \oplus E''\ .$$

(b) In the same way as in (a) one obtains

$$\Gamma^{(s)}_{l=2} = A_{1\mathrm{g}} \oplus E_{1\mathrm{g}} \oplus E_{2\mathrm{g}}\ .$$

5. With an electric field in the z direction, the symmetry group does not change and accordingly the level does not split. If the field points in the x direction, only two symmetries remain; the identity element and the mirror plane in which the axis lies. This is the group C_s, in which there are no degeneracies, so the level must split up. With (5.23) then results

$$\begin{aligned}n_A &= \frac{1}{2}(1\cdot 2+1\cdot 0) = 1\ ,\\ n_B &= \frac{1}{2}(1\cdot 2-1\cdot 0) = 1\ ,\end{aligned}$$

i.e. $\bar{\Gamma}^E \to \bar{\Gamma}^A \otimes \bar{\Gamma}^B$. Here we have used the fact that C_s has the same character table as C_2 in Table 6.1.

Chapter 9

1. Expressed by the components $\hat{x}_i$ of $\hat{\vec{r}}$ we have to show that

$$\hat{U}_{\tilde{D}} \cdot \hat{x}_i \cdot \hat{U}_{\tilde{D}}^{\dagger} = \sum_j D_{i,j} \hat{x}_j \ . \tag{B.7}$$

   This is equivalent to

$$\langle \vec{r} | \hat{U}_{\tilde{D}} \cdot \hat{x}_i \cdot \hat{U}_{\tilde{D}}^{\dagger} | \vec{r}' \rangle = \sum_j D_{i,j} \langle \vec{r} | \hat{x}_j | \vec{r}' \rangle \qquad \forall \vec{r}, \vec{r}' \ .$$

   We first evaluate the left hand side of this equation

$$\begin{aligned} \langle \vec{r} | \hat{U}_{\tilde{D}} \cdot \hat{x}_i \cdot \hat{U}_{\tilde{D}}^{\dagger} | \vec{r}' \rangle &= \langle \tilde{D} \cdot \vec{r} | \hat{x}_i | \underbrace{\tilde{D} \cdot \vec{r}'}_{=\sum_k [\sum_j D_{k,j} x'_j] \vec{e}_k} \rangle \\ &= \sum_j D_{i,j} x'_j \underbrace{\langle \tilde{D} \cdot \vec{r} | \tilde{D} \cdot \vec{r}' \rangle}_{=\delta(\vec{r} - \vec{r}')} \ . \end{aligned}$$

   This is obviously the right hand side of (B.7). $\surd$

2. We can use (9.18) to solve the problem. We only need the characters $\bar{\chi}$ of the orthogonal matrices in C_3 and D_3 using (3.5):

   (i) C_3 has the three classes $\{E\}, \{\delta_3\}, \{\delta_3^2\}$ for which

$$\begin{aligned} \bar{\chi}(E) &= 3 \ , \\ \bar{\chi}(\delta_3) &= 0 \ , \\ \bar{\chi}(\delta_3^2) &= 0 \ . \end{aligned}$$

   Hence,

$$n_1 = \frac{1}{3}(1 \cdot 3^2 + 1 \cdot 0^2 + 1 \cdot 0^2) = 3 \ .$$

   (ii) D_3 has the three classes $\{E\}, \{\delta_3, \delta_3^2\}, \{\delta_{2,1}, \delta_{2,2}, \delta_{2,3}\}$ for which

$$\begin{aligned} \bar{\chi}(E) &= 3 \ , \\ \bar{\chi}(\delta_3) = \bar{\chi}(\delta_3^2) &= 0 \ , \\ \bar{\chi}(\delta_{2,i}) &= -1 \ . \end{aligned}$$

   Hence,

$$n_1 = \frac{1}{6}(1 \cdot 3^2 + 2 \cdot 0^2 + 3 \cdot (-1)^2) = 2 \ .$$

3. The orthogonal matrices of this group are (with $z = 0$ being the mirror plane)

$$\tilde{D}(E) = \tilde{1} \ , \quad \tilde{D}(\delta_2) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \ .$$

With these matrices, we find exactly the same product representation as for the group C_2, so that the tensor has the same form as in (9.19).

4. We only have to evaluate (9.18), whereby we can take the characters of Table 7.1 from the line for the representation T_u. Herewith it follows

$$n_1 = \frac{1}{48}(1 \cdot 9 + 6 \cdot 1 + 3 \cdot 1 + 8 \cdot 0 + 6 \cdot 1 + 1 \cdot 9 + 3 \cdot 1 + 6 \cdot 1 + 8 \cdot 0 + 6 \cdot 1) = 1 \ . \surd$$

5. Since the group C_2 is a proper point group, nothing changes compared to the polarization tensor discussed in Sect. 9.3. The same applies to the group C_i, since the two minus signs in the product matrices of the inversion matrix cancel each other out.

Chapter 10

1. In both groups we find the same multiplication rules of the two irreducible representations A and B as in the group C_2. Thus, we find the same selection rules (i) and (ii) as discussed at the end of Sect. 10.4. The only thing left to be clarified is to which irreducible representations the operators and states belong.

   (i) In the case of the group C_i we have the situation that all operators and states belong to the representation B. Therefore all matrix elements vanish.

   (ii) In the case of the group C_s it is

$$p = A : |p_x\rangle \ , \ |p_y\rangle \ , \hat{x} \ , \ \hat{y}$$
$$p = B : |p_z\rangle \ , \ \hat{z} \ .$$

   Therefore, the non-vanishing matrix elements are

$$\langle [p_x, p_y]|[\hat{x}, \hat{y}]|[p_x, p_y]\rangle \ , \ \langle [p_x, p_y]|\hat{z}|p_z\rangle \ , \ \langle p_x|\hat{z}|[p_x, p_y]\rangle \ ,$$

   where the square brackets mean that both operators or states can be inserted.

2. (a) In Exercise 5 of Chap. 7 it is shown that the matrices of the group O_h are isomorphic to those of the irreducible representation T_u. As shown in Exercise 1 of Chap. 9, the three components $\hat{x}_i$ form a vector operator where the representation in the definition (9.22) is already irreducible. Hence, the three components $\hat{x}_i$ are irreducible in this case, i.e.

$$\hat{T}_{p,m_p,\lambda_p} = \hat{T}_{T_{1u},1,i} = \hat{x}_i \ .$$

Thus,

$$\langle p, \lambda | \hat{x}_i | p', \lambda' \rangle = \langle p, \lambda | \hat{T}_{\tilde{p},1,i} | p', \lambda' \rangle$$

with $\tilde{p} = T_{1u}$ is necessarily zero if

$$C(p, T_{1u} | p') = 0$$

i.e. if p' does not appear in the reduction of $\Gamma^{p \otimes T_{1u}}$. This can be found out with the multiplication Table 10.1. It turns out that $C(p, T_{1u}|p') = 0$ except for the cases

$$\begin{aligned}(p, p') &= (A_{1g}, T_{1u}) \\ &= (E_g, \{T_{1u}, T_{2u})\}) \,, \\ &= (T_{1g}, \{A_{1u}, E_u, T_{1u}, T_{2u}\}) \,, \\ &= (T_{2g}, \{A_{2u}, E_u, T_{1u}, T_{2u}\}) \,, \\ &= (T_{1u}, \{A_{1g}, E_g, T_{1g}, T_{2g}\}) \,.\end{aligned}$$

(b) $\hat{x}_i \cdot \hat{p}_j$ transform like

$$\begin{aligned}\hat{U}_{\tilde{D}} \cdot \hat{x}_i \cdot \hat{p}_j \cdot \hat{U}_{\tilde{D}}^{\dagger} &= \hat{U}_{\tilde{D}} \cdot \hat{x}_i \cdot \hat{U}_{\tilde{D}}^{\dagger} \cdot \hat{U}_{\tilde{D}} \cdot \hat{p}_j \cdot \hat{U}_{\tilde{D}}^{\dagger} \\ &= \sum_{k,l} D_{k,i} \cdot D_{l,j} \cdot \hat{x}_k \cdot \hat{p}_l\end{aligned}$$

i.e. like the components of a tensor operator of rank 2. To identify the occurring irreducible components, one has to reduce the product representation of T_{1u}, which leads to (see Table 10.1)

$$T_{1u} \otimes T_{1u} = A_{1g} \oplus E_g \oplus T_{2g} \oplus T_{1g} \,.$$

We can more or less guess the irreducible components by transferring the purely spatial representation functions in Table 7.1 into quadratic functions of $\hat{x}_i$ and $\hat{p}_j$. We skip the index $m_p = 1$ in the following since it is the same in all tensor components.

(i) A_{1g} :

$$\hat{T}_{A_{1g},1} = \sum_i \hat{x}_i \cdot \hat{p}_i \,.$$

(ii) E_g:

$$\begin{aligned}\hat{T}_{E_g,1} &= \hat{x}_1 \cdot \hat{p}_1 - \hat{x}_2 \cdot \hat{p}_2 \,, \\ \hat{T}_{E_g,2} &= 2\hat{x}_3 \cdot \hat{p}_3 - \hat{x}_1 \cdot \hat{p}_1 - \hat{x}_2 \cdot \hat{p}_2 \,.\end{aligned}$$

(iii) T_{2g}:

$$\hat{T}_{T_{2g},1} = \hat{x}_1 \cdot \hat{p}_2 + \hat{x}_2 \cdot \hat{p}_1 \ ,$$
$$\hat{T}_{T_{2g},2} = \hat{x}_1 \cdot \hat{p}_3 + \hat{x}_3 \cdot \hat{p}_1 \ ,$$
$$\hat{T}_{T_{2g},3} = \hat{x}_2 \cdot \hat{p}_3 + \hat{x}_3 \cdot \hat{p}_2 \ .$$

(iv) T_{1g}: The cubic spatial representation functions in (7.2) are of no help in this context. However, the same transformation behavior is seen in these three functions

$$\hat{T}_{T_{1g},1} = \hat{x}_2 \cdot \hat{p}_3 - \hat{x}_3 \cdot \hat{p}_2 \ ,$$
$$\hat{T}_{T_{1g},2} = \hat{x}_3 \cdot \hat{p}_1 - \hat{x}_1 \cdot \hat{p}_3 \ ,$$
$$\hat{T}_{T_{1g},3} = \hat{x}_1 \cdot \hat{p}_2 - \hat{x}_2 \cdot \hat{p}_1 \ .$$

These are the three components of the angular momentum.
The inversion of the linear equations in (i) and (ii) leads to

$$\hat{x}_1 \cdot \hat{p}_1 = \frac{1}{6}(2 \cdot \hat{T}_{A_{1g},1} + 3 \cdot \hat{T}_{E_g,1} - \hat{T}_{E_g,2}) \ ,$$
$$\hat{x}_2 \cdot \hat{p}_2 = \frac{1}{6}(2 \cdot \hat{T}_{A_{1g},1} - 3 \cdot \hat{T}_{E_g,1} - \hat{T}_{E_g,2}) \ ,$$
$$\hat{x}_3 \cdot \hat{p}_3 = \frac{1}{3}(\hat{T}_{A_{1g},1} + \hat{T}_{E_g,2}) \ .$$

In the same way, the inversion of the remaining 6 equations in (iii) and (iv) yields

$$\hat{x}_1 \cdot \hat{p}_2 = \frac{1}{2}(\hat{T}_{T_{2g},1} + \hat{T}_{T_{1g},3}) \ ,$$
$$\hat{x}_2 \cdot \hat{p}_1 = \frac{1}{2}(\hat{T}_{T_{2g},1} - \hat{T}_{T_{1g},3}) \ ,$$
$$\hat{x}_1 \cdot \hat{p}_3 = \frac{1}{2}(\hat{T}_{T_{2g},2} - \hat{T}_{T_{1g},2}) \ ,$$
$$\hat{x}_3 \cdot \hat{p}_1 = \frac{1}{2}(\hat{T}_{T_{2g},2} + \hat{T}_{T_{1g},2}) \ ,$$
$$\hat{x}_2 \cdot \hat{p}_3 = \frac{1}{2}(\hat{T}_{T_{2g},3} + \hat{T}_{T_{1g},1}) \ ,$$
$$\hat{x}_3 \cdot \hat{p}_2 = \frac{1}{2}(\hat{T}_{T_{2g},3} - \hat{T}_{T_{1g},1}) \ .$$

Chapter 11

1. The Hamiltonian matrix is

$$\begin{pmatrix} \epsilon & 0 & \mathrm{i}\xi & 0 \\ 0 & \epsilon & 0 & -\mathrm{i}\xi \\ -\mathrm{i}\xi & 0 & -\epsilon & 0 \\ 0 & \mathrm{i}\xi & 0 & -\epsilon \end{pmatrix}$$

and has the eigenvalues

$$E_{1,2} = -\sqrt{\epsilon^2 + \xi^2} \quad , \quad E_{3,4} = \sqrt{\epsilon^2 + \xi^2} \, .$$

For example, the eigenvectors of the eigenvalues $E_{1,2}$ are

$$|\psi\rangle_1 = \mathrm{i}\alpha|\xi, \downarrow\rangle + \beta|\eta, \downarrow\rangle \, ,$$
$$|\psi\rangle_2 = -\mathrm{i}\alpha|\xi, \uparrow\rangle + \beta|\eta, \uparrow\rangle \, ,$$

where the explicit form of α, β is not relevant. One now has again to go through all group operations $\hat{T}_a$, calculate the trace

$$\chi(a) = \sum_{i=1}^{2} {}_i\langle\Psi|\hat{T}_a|\Psi\rangle_i \, ,$$

and then compare this value with the values that result from the representation matrices (11.13)–(11.14). As an example, we consider the operation $a = \delta^+_{2,z}$: With

$$\hat{T}_{\delta^+_{2,z}}|\xi, \sigma\rangle = \mp\mathrm{i}|\xi, \sigma\rangle \, ,$$
$$\hat{T}_{\delta^+_{2,z}}|\eta, \sigma\rangle = \mp\mathrm{i}|\xi, \sigma\rangle \, ,$$

we find

$$\hat{T}_{\delta^+_{2,z}}|\psi\rangle_1 = \mathrm{i}|\psi\rangle_1 \, ,$$
$$\hat{T}_{\delta^+_{2,z}}|\psi\rangle_2 = -\mathrm{i}|\psi\rangle_2 \, .$$

Hence, $\chi_{\delta^+_{2,z}} = 0$, as it has to be the case.

2. With the matrices $\hat{T}_{\vec{\alpha}_i}$ in (11.7) we find

$$\tilde{T}_{\vec{\alpha}} = \frac{1}{\sqrt{2}} \begin{pmatrix} -\mathrm{i} & -\mathrm{i} \\ -\mathrm{i} & \mathrm{i} \end{pmatrix} \, .$$

Table B.6 Multiplication table of the group $\bar{C}_i$ which is isomorphic to the dihedral group D_2

	E	I	$\bar{E}$	$\bar{I}$
E	E	I	$\bar{E}$	$\bar{I}$
I	I	E	$\bar{I}$	$\bar{E}$
$\bar{E}$	$\bar{E}$	$\bar{I}$	E	I
$\bar{I}$	$\bar{I}$	$\bar{E}$	I	E

Table B.7 Character table of the double point group $\bar{C}_3$ ($\omega = e^{\pi i/3}$)

$\bar{C}_3$	E^+	δ_3^+	$(\delta_3^2)^+$	E^-	δ_3^-	$(\delta_3^2)^-$
$p=0$	1	1	1	1	1	1
$p=1$	1	ω	ω^2	-1	ω^{-2}	ω^{-1}
$p=2$	1	ω^2	ω^{-2}	1	ω^2	ω^{-2}
$p=3$	1	-1	1	-1	1	-1
$p=4$	1	ω^{-2}	ω^2	1	ω^{-2}	ω^2
$p=5$	1	ω^{-1}	ω^{-2}	-1	ω^2	ω

This belongs to a rotation vector

$$\vec{\alpha} = -\pi \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix} .$$

3. The multiplication table of the group $\bar{C}_i$ can be readily derived and is given in Table B.6. A comparison with Table 2.3 shows that $\bar{C}_i$ is isomorphic to D_2.
4. According to our discussion in Sect. 11.4, all elements a^+, a^- are in one class (except for the elements E^+, E^-, I^+, I^-). Thus we find

$$\begin{aligned} \bar{D}_{2h} = &\{E^+\} \cup \{E^-\} \cup \{I^+\} \cup \{I^-\} \cup \{C_2^+(z), C_2^-(z)\} \cup \{C_2^+(y), C_2^-(y)\} \\ &\cup \{C_2^+(x), C_2^-(x)\} \cup \{\rho^+(x,y), \rho^-(x,y)\} \cup \{\rho^+(x,z), \rho^-(x,z)\} \\ &\cup \{\rho^+(y,z), \rho^-(y,z)\} . \end{aligned}$$

5. Since the number of elements in $\bar{C}_3$ and C_6 is identical, we only need to show that there is a generating element in $\bar{C}_3$. This element is δ_3^+, because

$$(\delta_3^+)^2 = (\delta_3^2)^+ , \ (\delta_3^+)^3 = E^- , \ (\delta_3^+)^4 = \delta_3^- , \ (\delta_3^+)^5 = (\delta_3^2)^- , \ (\delta_3^+)^6 = E^+ . \surd$$

With (4.13) we can set up the character Table B.7. Thus, the spinor representations are $p = 1, 3, 5$.

Chapter 12

1. The successive application of two group elements to a spatial vector $\vec{r}$ leads to

$$\begin{aligned}\{\tilde{D}|\vec{a}\}\cdot\{\tilde{D}'|\vec{a}'\}\cdot\vec{r} &= \{\tilde{D}|\vec{a}\}(\tilde{D}'\cdot\vec{r}+\tilde{D}'\cdot\vec{a}') \\ &= \tilde{D}\cdot\tilde{D}'\cdot\vec{r}+\tilde{D}\cdot\tilde{D}'\cdot\vec{a}'+\tilde{D}\cdot\vec{a}\ .\end{aligned}$$

   Hence,

$$\{\tilde{D}|\vec{a}\}\cdot\{\tilde{D}'|\vec{a}'\} = \{\tilde{D}\cdot\tilde{D}'|\tilde{D}\cdot\tilde{D}'\cdot\vec{a}'+\tilde{D}\cdot\vec{a}\}\ .$$

   With the identity element $\{\tilde{1}|\vec{0}\}$ we then find

$$\{\tilde{D}|\vec{a}\}^{-1} = \{\tilde{D}^{-1}|-\tilde{D}\cdot\vec{a}\}\ .$$

Chapter 13

1. If we multiply (13.2) with $\vec{b}_j$, we find

$$\vec{b}_i'\cdot\vec{b}_j = \frac{2\pi}{V}(\vec{b}_k\times\vec{b}_l)\cdot\vec{b}_j\ .$$

   Since i, k, l are cyclic, it must be $i = j$ and thus (13.1) follows.
2. With (13.2) and (12.6), we find for the body-centered lattice the reciprocal basis vectors

$$\begin{aligned}\vec{b}_1' &\sim \vec{b}_2\times\vec{b}_3 \sim (0,1,1)\ , \\ \vec{b}_2' &\sim \vec{b}_3\times\vec{b}_1 \sim (1,0,1)\ , \\ b_3' &\sim \vec{b}_1\times\vec{b}_2 \sim (1,1,0)\ .\ \surd\end{aligned}$$

   Analogous with (12.7), we find for the face-center lattice

$$\begin{aligned}\vec{b}_1' &\sim \vec{b}_2\times\vec{b}_3 \sim (-1,1,1)\ , \\ \vec{b}_2' &\sim \vec{b}_3\times\vec{b}_1 \sim (1,-1,1)\ , \\ b_3' &\sim \vec{b}_1\times\vec{b}_2 \sim (1,1,-1)\ .\ \surd\end{aligned}$$

Chapter 14

1. The group $G_0(\vec{k})$ is C_{3v}. Degenerate are all vectors $\vec{G}$, for which

$$\vec{G}+2k(G_x+G_y+G_z)$$

Table B.8 Character table of plane-wave representation spaces for $\vec{k} = k(\vec{e}_x + \vec{e}_y + \vec{e}_z)$

	C_{4v}	E	$2C_3$	$3\sigma_v$
Γ_0	$\vec{G} = (0,0,0)$	1	1	1
Γ_1	$\vec{G} = \{(-1,0,0),(0,-1,0),(0,0,-1)\}$	3	0	1
Γ_2	$\vec{G} = \{(1,0,0),(0,1,0),(0,0,1)\}$	3	0	1
Γ_3	$\vec{G} = \{(-1,-1,0),(0,-1,-1),(-1,0,-1)\}$	3	0	1
Γ_4	$\vec{G} = \{(\pm1,\mp1,0),(0,\pm1,\mp1),(\pm1,0,\mp1)\}$	6	0	0

has the same value. The first 5 degenerate spaces are given in Table B.8. With (5.23) and the character table of C_{3v} (which is identical with that of D_3 given in Table 5.1) we can reduce the representations.

$$\begin{aligned}\Gamma_0 &= A_1 \ , \\ \Gamma_1 = \Gamma_2 = \Gamma_3 &= A_1 + E \ , \\ \Gamma_4 &= A_1 + A_2 + 2E \ .\end{aligned}$$

2. (a) We have a $\vec{k}$-dependent Hamilton matrix ($\epsilon_{i,j}(\vec{k}) \equiv \epsilon_{i,j}$)

$$\hat{H}_{\vec{k}} = \begin{pmatrix} \epsilon_{1,1} & \epsilon_{1,2} \\ \epsilon_{2,1} & \epsilon_{2,2} \end{pmatrix}$$

with eigenvalues

$$E_{\vec{k},\pm} = \frac{\epsilon_{1,1} + \epsilon_{2,2}}{2} \pm \sqrt{\frac{\epsilon_{1,1} - \epsilon_{2,2}}{4} + \epsilon_{1,2}^2} \equiv A \pm B \ ,$$

where

$$A = 2(t_\sigma + t_\delta) \sum_i \cos(k_i) \ ,$$

$$B = 4(t_\sigma + t_\delta)^2 \left(\sum_i \cos(k_i)^2 - \frac{1}{2} \sum_{i \neq j} \cos(k_i)\cos(k_j) \right) \ .$$

(b) The cubic point group operations applied to a vector $(k_x, k_y, k_z)^T$ leads to the 48 vectors $(\pm k_i, \pm k_j, \pm k_k)^T$ with all permutations of i, j, k. Obviously, the eigenenergies in (a) are invariant with respect to such transformations.

(c) A degeneracy is present here if $B = 0$. We consider the three symmetry lines

(i) $\vec{k} = k \cdot \vec{e}_x$:

$$B = 4(t_\sigma + t_\delta)^2 (1 - \cos(k))^2 \neq 0 \ .$$

Hence, there is no degeneracy. This is in agreement with our group theoretical expectations, because $G_0(\vec{k}) = C_{4v}$ and

$$E_g \underbrace{\longrightarrow}_{O_h \to C_{4v}} A_1 + A_2 \ .$$

(ii) $\vec{k} = k \cdot (\vec{e}_x + \vec{e}_y)$:

$$B = 4(t_\sigma + t_\delta)^2(1 - \cos k)^2 \neq 0 \ .$$

Hence, there is no degeneracy. This is in agreement with our group theoretical expectations, because $G_0(\vec{k}) = C_{2v}$ and

$$E_g \underbrace{\longrightarrow}_{O_h \to C_{2v}} A_1 + A_2 \ .$$

(iii) $\vec{k} = k(\vec{e}_x + \vec{e}_y + \vec{e}_z)$:

$$B = 0 \ .$$

Hence, there is a two-fold degeneracy. This is in agreement with our group theoretical expectations, because $G_0(\vec{k}) = C_{3v}$ and

$$E_g \underbrace{\longrightarrow}_{O_h \to C_{3v}} E \ .$$

The band structure is shown in Fig. B.9.

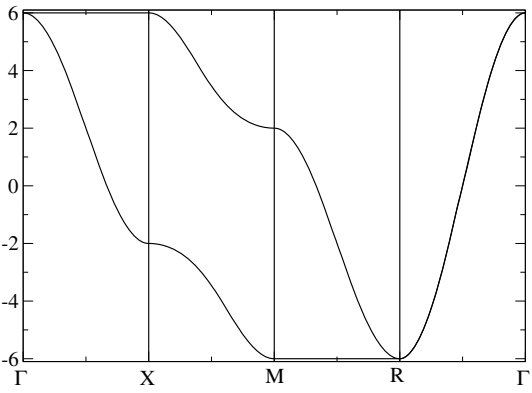

Fig. B.9 The band structure of two e_g-orbitals with nearest neighbor hopping

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